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XCII. *The Crystal Structure of Solid Methane.* *By* J. C. McLennan, *D.Sc.*, *F.R.S.*, *and* W. G. Plummer, *Ph.D.*

THE structure of the methane molecule has recently become a most interesting subject of discussion among theoretical physicists and chemists. According to some authorities, the results of recent work in the field of Atomic Physics are said to demand a pyramidal structure for the molecule instead of the hitherto universally accepted tetrahedral structure. In much of the literature upon the subject the state of the molecule under consideration is left entirely unspecified.

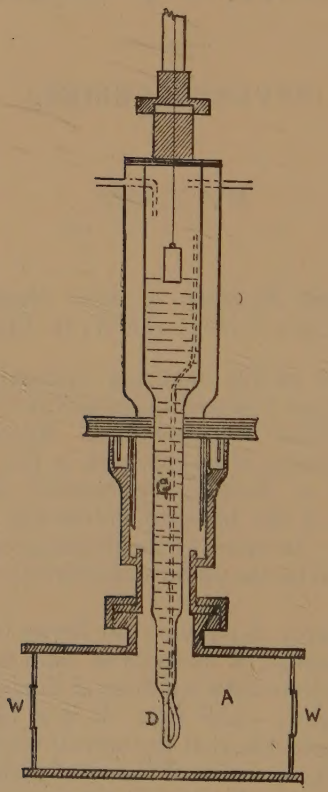
The present paper deals with an X-ray investigation by the "powder" method of analysis of solid methane at temperatures intermediate between those of liquid air (−190° C.) and liquid hydrogen (−255° C.). It is to be understood, in speaking of *the* molecule, that the *crystal* molecule is implied throughout, and the question of the relationship which it may bear to the chemical molecule will not be discussed here.

Any attempt at a complete determination of structure by the "powder" method alone must necessarily be open to a considerable amount of criticism, but at the present time the growth of single crystals of methane and their maintenance over a period sufficiently long for X-ray examination is not practicable; for this purpose a constant supply of liquid

* Communicated by the Authors.

hydrogen would be required. Hence, although it may not be permissible to regard the suggested structure as more than an approximation to the true one, the results of this examination definitely prove the existence of a cubic modification for solid methane over the temperature range of these experiments.

Fig. 1.



Apparatus.

A Debye-Scherrer type of camera, which closely resembled that described in a previous paper [1], was employed (fig. 1). After loading the cylindrical film-holder and placing it in the correct position in the camera (already determined by preliminary experiment), the edges of the loose lid were covered with a small quantity of a preparation of petrolatum

and beeswax, and the lid was firmly held in position by means of six clamps. The main chamber A was then evacuated for several hours by means of suitable pumps, a liquid-air trap having been inserted next to the chamber to prevent any mercury-vapour from reaching it. Next, the nickel-silver container G was filled with liquid hydrogen, and an interval of a quarter of an hour allowed for the cooling of the apparatus, after which a small quantity of pure methane was admitted to the main chamber from a side tube (the tap connecting the main chamber with the pumps having, of course, been closed just previously to introducing the methane). The deposition of crystals of solid methane on the outside of the copper capillary tube D could be observed through the window W, and when a layer of the desired thickness had formed, the crystalline powder was irradiated with X-radiation generated by a Shearer tube and suitably filtered to exclude β-lines. The rays passed into the camera through a lead slit 1 mm. wide which formed part of the camera, and was covered on the outside with thin aluminium foil. The exposure varied from 5 to 10 hours, with a current of approximately 6 milliamperes through the tube. Owing to the gradual decrease in thickness of the methane layer during the exposure, it was found advantageous to observe the layer carefully during the first stages, and to admit fresh methane when required. (Incidentally this procedure assisted in producing a more random orientation of crystals than would otherwise have been the case.)

Preparation of Methane.

Owing to the comparative ease with which most substances crystallize at liquid hydrogen temperatures, it is of the utmost importance that the methane employed shall be of the highest possible purity. Every precaution was taken to exclude impurities, and separate X-ray photographs under the same experimental conditions were taken of solid methane prepared by two different methods; the diffraction patterns obtained were apparently identical in the two cases.

In the first method methane was prepared by dropping a mixture of equal parts of methyl iodide and 95 per cent. methyl alcohol from a stoppered bottle into a large quantity of freshly-prepared zinc-copper couple. The gas, after being passed over another zinc-copper couple, was collected over distilled water and afterwards passed through tubes containing phosphorus pentoxide. Spectroscopic examination showed the gas to be free from nitrogen and possible iodide

impurity, and the only bands in evidence were those associated with the elements carbon and hydrogen.

The second method of preparation was from aluminium carbide and water. The flask, delivery tube, etc., were evacuated before commencing the reaction in order to save the trouble of displacing air in the apparatus. The gas was collected over distilled water and purified by bubbling it slowly through a solution of potassium dichromate and concentrated sulphuric acid. It was then passed through a caustic potash tube and two tubes containing phosphorus pentoxide. The final product was subjected to spectroscopic examination, and no bands other than those characteristic of carbon and hydrogen and CH compounds were observed.

After each exposure the communicating tap between the pumps and the main chamber was closed, and the frozen methane upon the capillary tube was allowed to warm up slowly until it reached the gaseous state. Samples of this methane were then examined spectroscopically for impurities, and the absence of nitrogen and oxygen bands indicated that air had not leaked into the chamber during the course of the experiment. This point was capable of further verification on development of the X-ray film, upon which no "powder" lines for those elements were observed.

Crystallographic Information.

The melting and boiling points of methane are given in the International Critical Tables[2] as $-184°$ C. and $-161°{\cdot}4$ C., respectively. In 1912 W. Wahl[3] found that pure methane crystallized very readily when cooled with liquid air under exhaust, and that the growth structures were always developed according to the hexahedron, and closely resembled those of ammonium chloride. The more rapid the crystallization, the finer were the resulting growth structures. The crystals were found to be isotropic; the molecule must therefore possess the four trigonal axes of symmetry characteristic of the cubic system, and consequently the valency directions must be assumed to make equal angles with one another. This argument applies also to the cubic forms of carbon tetrachloride, carbon tetrabromide, carbon tetraiodide, and tetramethylmethane.

Each of these compounds shows a low-temperature doubly-refracting modification; similarly for methane at very low (liquid hydrogen) temperatures Wahl[4] observed an enantiotropic transition into a doubly-refracting form.

Experimental Results.

For seven of the eight "powder" photographs obtained for solid methane the freezing agent employed was liquid hydrogen ; in the case of the remaining one liquid air under reduced pressure was used. Apart from slight displacements of the lines attributable to differences in thickness of the various layers, the X-ray patterns were apparently the same in all cases, and were typical of the cubic modification. Variation of the experimental conditions so as to favour the formation of the doubly-refracting modification observed by Wahl produced no change in the photographs. This is rather surprising, but the probable explanation is that, owing to inefficient heat insulation, a not inconsiderable temperature gradient existed between the inside of the copper capillary tube in contact with the liquid hydrogen and the exterior layers of crystals frozen upon the outside of this tube which were being photographed.

Four of the exposures were made with characteristic zinc K radiation and the remaining four with iron K_α-rays. The photographs obtained with the latter radiation were not so clear as those made with the zinc rays on account of the higher dispersion, and consequently broader lines, but the experimental spacings are in close agreement in the two cases. (Compare Tables I. and II. with Tables III. and IV.)

Table I. shows the derivation of the experimental spacings from measurements of the lines upon a typical "powder" photograph of solid methane (prepared in this case from methyl iodide and irradiated with zinc rays). As a very thick layer of methane was employed, the lines due to the copper of the capillary tube were scarcely visible, and have been excluded from the table. The approximate intensities of reflexion are indicated by the customary symbols : V.S., M., etc. The theoretical spacings in column 4, which correspond to the planes opposite them in column 5, have been calculated upon the assumption of a unit cube of edge 6·35 Å.

In order that more precise values of the longest spacings which occur might be obtained, together with a more accurate representation of the relative intensities of reflexion from the various planes, a very thin layer of solid methane was exposed (also to zinc radiation), for a shorter period ; the resulting spacings are given in Table II. In consequence of the reduced exposure, only four lines (in addition

TABLE I.—Methane Frozen with Liquid Hydrogen.

Zinc X-radiation, $\lambda K_{\alpha_1\alpha_2} = 1{\cdot}434$ Å. Copper filter.
Copper capillary tube. Exposure : $8\frac{1}{2}$ hr.
Correction for the thickness of the layer $= -0{\cdot}12$ cm.
Radius of the circular camera $= 3{\cdot}52$ cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
5·165 W. to M.	42° 03½′	1·070	1·075	135
4·805 W.	39 06½	1·137	1·123	440
4·44 M.	36 09	1·215	1·222	115 and 333
4·155 M.	33 48½	1·289	1·296	224
3·70 M.	30 08½	1·428	1·420	240
3·595 V.W.	29 15	1·468	1·456	133
3·30 V.W. to W.	26 51½	1·587	1·588	400
.....	.....	.....	1·835*	222
2·715 V.S.	22 06	1·905	1·914	113
2·295 V.S.	18 38	2·244	2·246	220
1·65 M.	13 26	3·09	3·18	200
1·395 V.S.	11 21½	3·64	3·67	111

* The presence of a reflexion from this plane cannot be established owing to a line from the copper capillary tube at a point corresponding to 1·801 Å.

TABLE II.—Methane Frozen with Liquid Hydrogen.

Zinc X-radiation, $\lambda K_{\alpha_1\alpha_2} = 1{\cdot}434$ Å. Copper filter.
Copper capillary tube. Exposure : $7\frac{1}{4}$ hr.
Correction for the thickness of the layer $= -0{\cdot}07$ cm.
Radius of the circular camera $= 3{\cdot}52$ cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
2·705 M. to S.	22° 01′	1·913	1·914	113
2·30 V.S.	18 43	2·235	2·246	220
1·62 M.	13 11	3·144	3·176	200
1·39 V.S.	11 19	3·655	3·667	111

to those given by the copper tube, which have been omitted from the table), were sufficiently intense to be measurable ; in this case the methane was prepared from aluminium carbide.

The spacings resulting from the measurement of two other films are derived in Tables III. and IV.; the remaining photographs have also been measured, and give, within the limits of experimental error, similar values.

TABLE III.—Methane Frozen with Liquid Air under Reduced Pressure.

Iron X-radiation, $\lambda K_{\alpha_1\alpha_2} = 1{\cdot}934$ Å.
Copper capillary tube. Exposure: 6 hr.
Correction for the thickness of the layer = − 0·16 cm.
Radius of the circular camera = 3·52 cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
4·64 W. to M.	37° 45½′	1·58	1·588	400
3·71 W. to M.	30 12	1·92	1·914	113
3·12 W. to M.	25 24	2·25	2·246	220
2·25 W.	18 19	3·08	3·176	200
1·88 M.	15 18	3·66	3·667	111

TABLE IV.—Methane Frozen with Liquid Hydrogen.

Iron X-radiation, $\lambda K_{\alpha_1\alpha_2} = 1{\cdot}934$ Å. Manganese filter.
Copper capillary tube. Exposure: 5½ hr.
Correction for the thickness of the layer = − 0·09 cm.
Radius of the circular camera = 3·52 cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
3·74 M.	30° 27′	1·91	1·914	113
3·11 M.	25 19	2·26	2·246	220
2·24 M.	18 13½	3·09*	3·176	200
1·89 M. to S.	15 23	3·65	3·667	111

* This line was particularly broad, and difficult to measure accurately.

Returning to Table I., the experimental spacings in column 3 are seen to be in very close agreement with those calculated for a face-centred cubic cell of edge 6·35 Å., which are given in column 4. Within the range of spacings shown, the only irregularity is the indefiniteness as to whether there is a reflexion from the (222) plane corresponding to 1·835 Å.; if such a reflexion exists, it is indistinguishable in the photographs from a line corresponding to 1·801 Å., for which the copper capillary tube is

responsible. (It was intended to settle this point by making an exposure with a capillary tube of some suitable metal other than copper.) Further, all planes which do not satisfy the condition for a face-centred lattice are absent. The density of liquid methane at approximately its boiling-point has been given as 0·415 gm./c.c. [5], and if this be used as an approximation to the density of the solid, then :

$$\text{No. of molecules per unit cell} = n = \frac{0{\cdot}415(6{\cdot}35)^3}{16{\cdot}03\,.\,1{\cdot}649} = 4{\cdot}02\,;$$

that is, there are four molecules per unit cell. There are no abnormal spacings except those demanded by a face-centred lattice, hence all the following space-groups have to be considered :

$$T^2,\ T_h^3,\ T_d^2,\ O^3,\ O_h^5.$$

If the further assumption is made that all the carbon atoms are crystallographically identical, and that all the hydrogen atoms are identical in this sense, only two of these, T^2 and T_d^2 give four equivalent positions for the carbon atoms and sixteen equivalent positions for the hydrogens [6]. In either case the four carbons in the positions of fourfold symmetry without any degrees of freedom will have coordinates :

$$000,\ 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{2}0\tfrac{1}{2},\ \tfrac{1}{2}\tfrac{1}{2}0\,;$$

the carbons themselves having symmetry T in the case of the space-group T^2, and T_d for the space-group T_d^2. The sixteen hydrogens in positions of 16-fold symmetry with one degree of freedom u will have coordinates :

$u,\ u,\ u\,;\ u,\ \bar{u},\ \bar{u}\,;\ \bar{u},\ u,\ \bar{u}\,;\ \bar{u},\ \bar{u},\ u\,;$
$u,\ u+\tfrac{1}{2},\ u+\tfrac{1}{2}\,;\ u,\ \tfrac{1}{2}-u,\ \tfrac{1}{2}-u\,;\ \bar{u},\ u+\tfrac{1}{2},\ \tfrac{1}{2}-u\,;\ \bar{u},\ \tfrac{1}{2}-u,\ u+\tfrac{1}{2}\,;$
$u+\tfrac{1}{2},\ u,\ u+\tfrac{1}{2}\,;\ u+\tfrac{1}{2},\ \bar{u},\ \tfrac{1}{2}-u\,;\ \tfrac{1}{2}-u,\ u,\ \tfrac{1}{2}-u\,;\ \tfrac{1}{2}-u,\ \bar{u},\ u+\tfrac{1}{2}\,;$
$u+\tfrac{1}{2},\ u+\tfrac{1}{2},\ u\,;\ u+\tfrac{1}{2},\ \tfrac{1}{2}-u,\ \bar{u}\,;\ \tfrac{1}{2}-u,\ u+\tfrac{1}{2},\ \bar{u}\,;\ \tfrac{1}{2}-u,\ \tfrac{1}{2}-u,\ u.$

If the space-group T^2 is under consideration, the symmetry of the hydrogen atom itself will be C_3 ; but if the correct space-group is T_d^2 this symmetry will be C_{3v}.

The next step is to calculate the resulting theoretical intensities for the various values of the parameter u, and to ascertain which particular value of u gives the best agreement with the observed intensities. This work has been summarized in Table V., which shows the intensities of the various planes relative to the standard value 15 arbitrarily chosen for the (111) plane. The formula employed was

$$\text{Intensity} \propto Q\,.\,Z\,.\,S^2,$$

where S is the structure factor, which depends upon the

Table V.

Intensities Calculated for Various Values of the Parameter u.

Plane.	Q factor.	Z.	Intensity relative to that of the (111) plane, taken as 15.							Experimental intensity.
			$u=0$.	$u=0{\cdot}1$.	$u=0{\cdot}13$.	$u=0{\cdot}15$.	$u=0{\cdot}18$.	$u=0{\cdot}2$.	$u=0{\cdot}22$.	
440	$2\frac{1}{4}$	12	2·1	2·3	3·9	3·1	1·6	1·7	0·3	W.
115 & 333	$2\frac{1}{2}$	24 & 8	6·3	1·8	3·1	4·2	4·8	4·3	4·5	M.
224	$2\frac{1}{2}$	24	4·7	2·6	3·2	3·4	3·7	4·6	6·7	M.
240	3	12 or 24	2·8 or 5·7	1·5 or 3·0	2·0 or 4·1	2·7 or 5·3	2·9 or 5·9	1·4 or 2·8	0·6 or 1·2	M.
133	3	24	5·7	3·6	6·0	7·6	7·3	5·4	5·2	V.W.
400	$3\frac{1}{2}$	6	1·7	0·2	0·1	0·2	1·0	1·8	0·2	V.W. to W.
222	5	8	3·2	2·1	2·7	2·9	1·8	1·0	0·6	—
113	$5\frac{3}{4}$	24	11	4·5	4·4	4·6	6·3	8·2	9·6	V.S.
220	$8\frac{1}{2}$	12	8·1	4·8	5·2	6·3	9·6	12	1·2	V.S.
200	$17\frac{1}{2}$	6	8·3	6·2	5·0	3·5	2·1	1·3	0·8	M.
111	$23\frac{3}{4}$	8	15	15	15	15	15	15	15	V.S.

geometrical positions of the atoms and on their scattering-powers. As a first approximation, the latter were taken as proportional to the atomic numbers (C=6, H=1). The Q factor referred to in column 2 was calculated from

$$Q = \frac{1+\cos^2 2\theta}{2} \cdot \frac{1}{\sin^2\theta \cdot \cos\theta},$$

where θ is the glancing-angle.

The "Z" number represents the number of cooperating planes, and it will be noted that, in the case of the (240) plane, its value may be 12 or 24, according to whether the space-group is T_2 or T_d^2 respectively; hence, until the question of the correct space-group is settled, there will be for this plane two possible values for the resulting intensities. The temperature factor was not introduced into the intensity formula, as its effect should be almost negligible at the temperatures used in these experiments.

The particular case of $u=0$ is equivalent to disregarding entirely the scattering effect of the hydrogen atoms; or, alternatively, to considering that the four valency electrons from the four hydrogen atoms in the CH_4 molecule have joined the four outer electrons belonging to the carbon atom, thus forming a scattering system of eight electrons per molecule, which should be a stable configuration. It is extremely probable that such systems would be very nearly identical for each molecule throughout the structure; hence each system might be regarded, for the purpose of scattering, as the true structural unit, and might conveniently be supposed to be concentrated at the centre of the carbon nucleus (since it is the same for each molecule). If this be the case, the X-ray results will give no indication of the distance from the centre of the carbon nucleus to the orbit in which the electrons rotate; it will only be possible to determine the distance from one molecule to the next. A comparison of the experimental and theoretical intensities for the various values of the parameter u in Table V. shows that no value of u gives very good agreement, but $u=0$ apparently gives the nearest correspondence, though the observed reflexion from the (133) plane is too weak. A more encouraging agreement is obtained if, in the calculation of the theoretical intensities, the scattering effect of the hydrogen atoms be neglected ($u=0$), and the factor f given by Ponte[7] for reflecting power of the carbon atom for high-frequency rays (which varies with the spacing) be used instead of the constant factor 6 for the carbon atom. The values of f given in Table VI. are taken from Curve III. of Ponte's

paper, and the square of this factor has been used in the calculation of the theoretical intensities given in column 3 of the table; the Lorentz factor, the geometrical structure factor, and the factor for the number of cooperating planes have also been taken into consideration in this calculation. With the exception of the reflexions from the (111), (200), and (133) planes, which are not sufficiently strong, the observed intensities (taken from Table I.) agree quite well with the corresponding theoretical values. It is only fair to add that the lines corresponding to the (111) and (220) planes in the photographs obtained with zinc radiation (Tables I. and II.)

Table VI.

Calculated Intensities using the Ponte Factor.

Plane.	f.	Theoretical intensity proportional to:	Observed intensity (from Table I.).
440	1.5	1·0	W.
115 & 333	1·6	3·4	M.
224	1·73	3·0	M.
240	1·90	2·1 or 4·3	M.
133	1·95	4·5	V.W.
400	2·15	1·6	V.W. to W.
222	2·45	4·0	—
113	2·6	15	V.S.
220	3·0	15	V.S.
200	4·05	28	M.
111	4·5	63	V.S.

V.S.=Very strong; S.=Strong; M.=Moderately strong; W.=Weak; V.W. to W.=Very weak to weak; V.W.=Very weak.

are so strong that no further blackening of the film would be detectable, and the next stage would be reversal; this might explain why the (111) reflexion is not stronger in the photographs than that from the (220) plane. However, the comparative weakness of the (200) reflexion still remains unexplained, but in all the photographs the line corresponding to this plane is noticeably broader than the remainder, and this fact cannot very well be taken into account in ordinary eye-estimations of the relative intensities of the lines.

This analysis of intensities would therefore appear to support the idea, to which reference has already been made,

of stable and practically identical scattering systems for each molecule of methane throughout the structure, the molecules being arranged upon a face-centred lattice. It is difficult to interpret in any other way the fact that the most satisfactory agreement of intensities is obtained when $u=0$.

In any case, this investigation confirms the conclusion arrived at by Wahl, by optical methods, that a cubic form of methane really exists, and it disproves the view recently expressed in several papers that the structure of the methane molecule cannot be cubic, but that it must be pyramidal. No evidence of the existence of a pyramidal modification has been found in this work, but its probable existence is not disputed.

The chief arguments put forward in opposition to the existence of a cubic structure for methane have been classified by V. Henri [8] under the following heads :—

(1) The scattering of light by methane (studied by Cabannes).
(2) Its absorption spectrum (examined by Cooley and Dennison).
(3) The emission spectra of the carbon atom (examined by Millikan and Bowen).
(4). The crystal structure of methane derivatives (in particular penta-erythritol, examined by Mark and Weissenberg, and Huggins and Hendricks).
(5) Calculation of the potential energy of the methane molecule (made by Guillemin, and Van Arkel and De Boer).

If it is admitted that methane can exist in two different modifications, it is surely quite impossible to predict which of these forms is assumed for the particular conditions of experiment in cases (1) and (2). In either case the experimental technique is very difficult, and it is even possible that both forms exist together under such conditions. And in case (4) the selection of pentaerythritol as a substance whose structure might be characteristic of that of methane seems rather unfortunate in view of the fact that regular modifications of its more closely-related compounds, carbon tetrachloride, tetrabromide, and tetraiodide, are known to exist, especially as carbon tetrachloride has been shown to possess only a negligible dipole moment. The calculation of the potential energies of the pyramidal and tetrahedral configurations of the methane molecule in case (5) involves the use of the numerical data obtained from the work on the absorption spectrum in (2), and the authors of the two

papers[9,10] dealing with this subject are in disagreement as to which is the more stable configuration, owing to differences in original assumptions. With regard to case (3), it has been shown, by examination of the emission spectra of the carbon atom, that in neutral carbon the four valencies are not equal, but that there are two (2, 2) and two (2, 1) electrons. In methane, however, if the four electrons belonging to the hydrogen atoms join these four, and form a stable system of eight (similar to the neon electron configuration), as the analysis of intensities in this paper would seem to indicate, this objection to the existence of a cubic modification is removed. The results of this investigation therefore leave little doubt that a regular form of methane does actually exist, and this conclusion is supported by the recent work of Weissenberg[11], who has shown from theoretical considerations that for substances of the type $C\alpha_4$ the occurrence of the electrically symmetrical molecule is to be expected just as frequently as that of the pyramidal type.

A complete list of references to papers dealing with this subject is unnecessary, as excellent lists have already been prepared by the authors of the following papers :—

K. Lonsdale (*née* Yardley), Phil. Mag. vi. p. 433 (1928).
J. K. Morse, Proc. Nat. Acad. Sci. xiv. (Feb. 1928).

Note.—Though my collaborator has kindly signified that he wishes my name to be associated with this paper, I desire to say the details have been practically all worked out by him. The research is one of a number I planned and initiated, but the growing pressure of other investigations precluded my following up the work as closely as I was able to do in the early stages. I should add that throughout we had much valuable help from Mr. J. O. Wilhelm in the liquefaction of air and hydrogen. The investigation is one of the many made possible with the cryogenic equipment secured through the help of the Carnegie Corporation, the National Research Council of Canada, and the University of Toronto.—J. C. McLennan.

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XCIII. *The E.M.F. of Thermal Agitation.* *By* E. K. Sandeman, *Ph.D.*, *and* L. H. Bedford, *M.A.**

AS an incident in a certain investigation carried out for the Laboratories of the International Standard Electric Corporation, some work of J. B. Johnson on the e.m.f. of thermal agitation (Physical Review, vol. xxxii., July 1928, pp 97–109) has been verified. The accuracy of the results is not so great as his, but it is thought that the confirmatory evidence obtained is of value.

A simple precision formula has been derived, which it is believed will prove useful for many practical purposes in calculating quickly and accurately in R.M.S. microvolts the magnitude of noise disturbance which occurs on the grid of the first stage of any amplifier. This formula is admittedly only applicable under certain limiting conditions, but fortunately those limiting conditions are the ones which occur most often in practice. In practice it is usually required to amplify uniformly a given band of frequencies, and the impedance between the grid and filament of the first valve is usually a pure resistance shunted by a capacity, within the pass-band of the system The truth of this has been verified for audio-frequency systems using good input transformers to the grid of the first stage.

With the above qualifications the noise in microvolts on the grid of the first valve is given by:—

$$N = \frac{JT^{\frac{1}{2}}}{\sqrt{2\pi C}} \sqrt{\tan^{-1} 2\pi RCF_2 - \tan^{-1} 2\pi RCF_1} \quad . \quad (1)$$

(the inverse tangents being expressed in radians),

* Communicated by the Authors.

where

$J = 7{\cdot}4 \times 10^{-6}$ a constant,

T = the absolute temperature, normally about 293,

R = the total grid-filament resistance in ohms (= reciprocal of sum of conductance external and internal to the valve),

C = the total grid-filament capacity in farads,

F_1 and F_2 = the frequency limits of the pass range of the receiving system in cycles per second.

J is derived directly from Boltzmann's constant K by the formula

$$J = 200\sqrt{10K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Taking the accepted value of K (Int. Crit. Tables, v. 1, p. 18) as $1{\cdot}372 \times 10^{-16}$,

$$J = 200 \times 10^{-8} \times \sqrt{13{\cdot}73}$$
$$= 7{\cdot}4 \times 10^{-6}.$$

Example.

T = 293,

R = 100,000 ohms,

C = 150 micro-microfarads,

F_1 = 30 cycles per second,

F_2 = 7000 cycles per second,

$$N = \frac{7{\cdot}4 \times 10^{-6} \times 17{\cdot}1}{\sqrt{150 \times 10^{-12} \times 6{\cdot}28}} \sqrt{\tan^{-1}6{\cdot}28 \times 10^5 \times 150 \times 10^{-12} \times 7000 - \tan^{-1}6{\cdot}28 \times 10^5 \times 150 \times 10^{-12} \times 30}$$

$$= 4{\cdot}12 \times \sqrt{\tan^{-1}0{\cdot}66 - \tan^{-1}0{\cdot}00283}$$

$$= 4{\cdot}12 \times \sqrt{0{\cdot}584 - 0{\cdot}00283}$$

$$= 4{\cdot}12 \times 0{\cdot}76$$

$$= 3{\cdot}1 \text{ microvolts (slide rule).}$$

It is here evident that the second term under the root is negligible. If the value of R is increased indefinitely, the first term approaches a limiting value asymptotically and the second term also approaches the same value, lagging behind the first. The result is that as the resistance is increased

indefinitely the potential variation across the resistance due to the thermal agitation increases to a maximum and then decreases. This effect is shown very well in Johnson's fig. 5 (Physical Review, July 1928, p. 103). In our experiments, owing to the low value of F_1 the lower cut-off of the amplifier system, we never reached such a maximum even by increasing R to the grid-filament conductance of the valves (about 50 megohms).

Apparatus.

The equipment consisted of a four-stage resistance-coupled amplifier using 4102–E ($\mu = 30$) valves, followed by a three-stage coil-coupled amplifier giving substantially uniform amplification in the range 30–7000 cycles. The gain of the last amplifier was adjustable in steps of 3 decibels, and was used on about half gain.

The working amplification was about two million on a voltage basis from the grid of the first valve to the plate of the last. The output was observed by means of a rectifier valve and a milliammeter, the input to the rectifier containing a potentiometer adjustable in steps of 2 decibels.

The first stage of the system was mounted on a small wooden platform slung on rubber bands in a tea-box to eliminate vibration. The foil of the tea-box afforded screening. Acoustic quietness was secured by conducting the experiments in the country, and sufficient freedom from electrical pick up was obtained by switching off the light circuit at the main.

A calibrating voltage of 1000 cycles was applied from a reed oscillator, its output being measured by a thermocouple and applied to a 600 ohm attenuator, variable in steps of 0·2 β1. The output from the attenuator was connected to a transition network having the ratio 600 : 3 ohms, and the voltage output from this was applied to the grid of the first valve through a balanced shielded coil (SS. 5115–1 Repeating Coil made by Messrs. Standard Telephones and Cables). We have found this coil invaluable for this kind of work, as it is balanced to a very high degree of accuracy, and its transmission characteristics from 30 to 10,000 cycles are excellent, *e. g.*, when operating in a 600-ohm circuit the loss in this range does not exceed $1\frac{1}{2}$ decibels. As used in the circuit here described the loss was quite negligible. The stray field of such coils is also small, as they are toroidally wound, but with magnifications of the order used it was necessary to separate the input coil from the coils in the

second amplifier by about fifteen feet to reduce the effects of reaction. As the circuit was originally set up to obtain comparative noise figures on different valves the presence of reaction was not serious, and it was only when idle curiosity prompted us to see how near our value of Boltzmann's constant came to the correct value that we took steps to get a better value by eliminating sources of error.

The method of measurement was to insert any value of input resistance, adjust the gain to give a convenient deflexion on the output meter, and then decrease the rectifier sensitivity by 10 decibels on its potentiometer before applying the calibrating voltage, which was adjusted until the same deflexion was again obtained. The second deflexion was therefore due to the calibrating voltage C plus the noise voltage N_1, and this deflexion corresponds to a voltage V_c, which is 10TU above N_1

$$\therefore \quad V_c = \sqrt{N_1^2 + C^2} = 3{\cdot}16\ N_1$$

$$\therefore \quad N_1 = \frac{1}{3}\,C \text{ instead of } \frac{1}{3{\cdot}16}\,C,$$

which was the original assumption made, and would be the case if the noise voltage were eliminated while the calibrating voltage was being applied. The correction was not considered worth while taking account of at first, but the accuracy of our results, which, it must be admitted, surprised us, is such as to warrant it being applied. The observed values of J tabulated below must therefore be multiplied by $\frac{3{\cdot}16}{3}$ to give the corrected figure.

As in Johnson's work, the plate noise has been subtracted from the total observed noise results before recording them as N. The plate noise was very nearly equivalent to one microvolt on the grid and is subtracted from N_1 by taking the square root of the difference of the squares to give N.

Example of Determinations of J.

Valve 4102–E Serial No. S. 45.
Room temperature = 20° C. = 293° K.
C = 116$\mu\mu$F (measured on a capacity and conductance bridge) + the estimated capacity of the leads 15$\mu\mu$F.
= 131$\mu\mu$F.
F_2 = approximately 7000 p.p.s.
F_1 = approximately 30 p.p.s.

The second term under the root may be neglected, so that the exact value of the lower cut-off of the amplifier is here

unimportant. Examination of the formulæ shows that it is also very insensitive to variations of F_2, while errors in C are halved.

$$\frac{T}{\sqrt{2\pi C}} = \frac{17{\cdot}13}{\sqrt{2\pi \times 131 \times 10^{-12}}} = 597 \times 10^{-6}.$$

The remainder of the results and calculation may conveniently be tabulated :—

R.	N.	$\mathrm{Tan}^{-1}2\pi RCF_2$.	$\sqrt{\mathrm{Tan}^{-1}2\pi RCF_2}$.	$J \times 10^6$.
10^4	·895	·0576	·24	6·25
$5{\cdot}5 . 10^4$	2·19	·303	·55	6·66
10^5	2·5	·523	·723	5·8
$2{\cdot}5 . 10^5$	3·72	·963	·982	6·33
$6{\cdot}10^5$	4·8	1·29	1·135	7·1
10^6	5·1	1·39	1·18	7·23

In the table below are given three sets of observed values of $J \times 10^6$:

(*a*) From measurements made on four valves with circuit as originally set up (*i. e.*, with a small amount of reaction present).

(*b*) From measurements made on one valve after steps had been taken to reduce the reaction.

(*c*) As (*b*), but with a filter inserted in the receiving system having a cut-off at 2200 cycles per second.

		a.				*b.*	*c.*
R.	Valve	4102-E S. 45	4102-E S. 48	102-E E.	102-E B.	102-E B.	102-E B.
10^4		6·25	7·00	7·00	8·00	—	—
$5{\cdot}5 . 10^5$		6·66	7·66	7·80	3·50	6·22	5·70
10^5		5·80	7·10	7·28	7·70	8·20	8·40
$2{\cdot}5 . 10^5$		6·33	6·27	6·60	6·76	7·10	7·90
$6{\cdot}10^5$		7·10	5·63	6·12	5·77	6·97	7·20
10^6		7·23	5·50	6·02	5·30	—	—
Averages			6·52			7·1	7·3
Averages $\times \frac{3{\cdot}16}{3}$ ..			6·86			7·47	7·7
Derived value of Boltzmann's constant $\times 10^{16}$.			1·17			1·39	1·48

The correct value of Boltzmann's constant has already been quoted as $1{\cdot}372 \times 10^{-16}$.

The improved value of Boltzmann's constant given under (*b*), obtained after steps had been taken to reduce reaction, was distinctly encouraging, and prompted us to make some effort to locate the upper cut-off more certainly. For this purpose a filter having an upper cut-off at 2200 cycles was introduced between the output of this amplifier and the rectifier. It was, however, unbalanced and unscreened, and introduced considerable reaction. Screening reduced the reaction very largely, but it is possible that reaction still persisted due to the unbalance. It will be appreciated that we were more interested in the practical confirmation of the existence of the e.m.f. of thermal agitation than in a precise determination of a constant which was already known. We considered that the above results in conjunction with those immediately below were sufficient evidence for our purpose, and it was for this reason we did not press investigation further.

As an additional check, the effect of cooling a number of grid leaks with liquid air was tried. The results are given below, the values of microvolts on the grid being completely corrected as described above. The grid leak was connected to the input of the first valve by long leads,

Effect of Cooling Grid Leaks with Liquid Air.

Type of Grid Leak.	Temperature. Centigrade.	Resistance. Megohms.	Observed microvolts.	Reduction Ratio.	Remarks.
Davohm	20	·95	3·29	1·48	Wire wound.
„	−180	·93	2·22		
Mullard	20	1·18	3·25	1·42	
„	−180	3·9	2·35		
Western Electric.	20	·40	3·27	1·73	
	−180	·67	1·89		
Lynch	20	·53	3·55	1·5	
„	−180	·89	2·37		
Ediswan	20	1·05	4·13	1·53	
„	−180	2·92	2·69		
Dumetohm (1)	20	·94	3·51	1·67	
„	−180	1·87	2·11		
Dumetohm (2)	20	·24	3·33	1·42	Gave same value on warming up after cooling.
„	−180	·48	2·35		
Dumetohm (3)	20	·665	3·92	1·61	
„	−180	1·015	2·43		

and placed in a test-tube which was lowered into a Dewar flask containing liquid air. The Dewar flask was placed inside the tea-box which held the first stage of the amplifier.

If the observed potential variation is due to thermal agitation, then it would seem reasonable to expect that its value would be proportional to the square root of the absolute temperature (since energy is proportional to the absolute temperature and to voltage squared). In this case the expected reduction ratio in the absence of other sources of potential variation

$$=\sqrt{\frac{273+20}{273-180}}=1{\cdot}775.$$

In every case the observed reduction is less than this value. One possible explanation of this would be given by the presence of Johnson noise in the grid filament conductance of the valve itself (which was not cooled), which, adding to the noise in the resistance, makes the reduction on cooling appear smaller. Another and more obvious explanation, which, however, is not applicable in the case of the wire wound (Davohm) resistance, is that the value of the resistance increases on cooling. The diminution in reduction ratio due to this is, however, small. When $R=50{,}000$ ohms, $C=100$ micro-microfarads, $F_1=30$ cycles, and $F_2=7000$ cycles, the increase in N by doubling R, as given by equation (1), is 1·09 times. It is unfortunate for this theory that the value of reduction ratio with the wire-wound resistance was the smallest observed.

Appendix I.

Derivation of formula for N, *the potential difference generated across the terminals of a resistance* R *shunted by a capacity* C *due to the E.M.F. of thermal agitation.*

The potential difference required differs from the E.M.F. on account of the load constituted by the inevitable capacity. This load is a function of frequency, and to handle the problem it is necessary to consider the noise E.M.F. as made up of a great number of small frequency bands ; the noise E.M.F. in the range of angular frequency n_1 to n_2 is therefore written,

$$e=\int_{n_1}^{n_2} \mathrm{E}_n \cos nt \, . \, dn \qquad (n_2>n_1).$$

Lemma.

Each elemental frequency band contributes to the mean square voltage just like a distinct frequency,

i. e. $$d(\mathrm{E}^2) = (\Delta \mathrm{E})^2,$$

where the left-hand side is the increment of mean square voltage corresponding to an increment dn in angular frequency, and the right-hand side is the square of the R.M.S. voltage in angular frequency range n to $n+dn$.

By the mean square voltage is meant the non-oscillating part of

$$\left(\int_{n_1}^{n_2} \mathrm{E}_n \cos nt\, dn\right)^2.$$

This $$= \int_{n_1}^{n_2} dn \int_{n_1}^{n_2} dn' \mathrm{E}_n \mathrm{E}_{n'} \cos nt \cos n't,$$

$$= \int_{n_1}^{n_2} dn \int_{n_1}^{n_2} dn' \tfrac{1}{2} \mathrm{E}_n \mathrm{E}_{n'} (\cos \overline{n+n'}t + \cos \overline{n-n'}t).$$

To write down the non-oscillating part it is necessary to select the contributions of zero frequency; such contributions occur only when $n' = n$. Putting in this condition we find that the non-oscillating part of the mean square voltage is given by

$$\mathrm{E}^2 = \int_{n_1}^{n_2} \tfrac{1}{2} \mathrm{E}_n^2 dn^2.$$

But $\frac{1}{2}\mathrm{E}_n^2 dn^2$ is the square of the R.M.S. voltage in the frequency range n to $n+dn$, which is by definition $(\Delta \mathrm{E})^2$.

$$\therefore \quad \mathrm{E}^2 = \int_{n_1}^{n_2} (\Delta \mathrm{E})^2,$$

and $$d\mathrm{E}^2 = (\Delta \mathrm{E})^2.$$

Applying this to the case of Johnson noise, Johnson states that the mean square E.M.F. of thermal agitation is uniformly distributed throughout the frequency spectrum, and that it is proportional to the absolute temperature and to the resistance in which it occurs—that is,

$$\mathrm{E}^2 = \mathrm{J}^2 \mathrm{TRF},$$

where F is the width of the frequency band.

Thus $$d\mathrm{E}^2 = \mathrm{J}^2 \mathrm{TR} dF$$

and so $$(\Delta \mathrm{E})^2 = \mathrm{J}^2 \mathrm{TR} dF.$$

Now let ΔN represent the p.d. across the terminals of the resistance R due to the E.M.F. ΔE. We have,

$$\Delta N = \Delta E \frac{\frac{1}{nC}}{\sqrt{R^2 + \frac{1}{n^2C^2}}},$$

and
$$N^2 = \int d(N^2) = \int (\Delta N)^2$$

$$= \int (\Delta E)^2 \frac{\frac{1}{n^2C^2}}{R^2 + \frac{1}{n^2C^2}}$$

$$= J^2TR \int_{F_1}^{F_2} \frac{\frac{1}{n^2C^2}}{R^2 + \frac{1}{n^2C^2}} dF$$

$$= J^2TR \int_{F_1}^{F_2} \frac{1}{1 + 4\pi^2C^2R^2F^2} dF$$

$$= \frac{J^2T}{2\pi C} \left[\tan^{-1} 2\pi CRF_2 - \tan^{-1} 2\pi CRF_1 \right].$$

$$\therefore \quad N = \frac{JT^{\frac{1}{2}}}{\sqrt{2\pi C}} \sqrt{\tan^{-1} 2\pi CRF_2 - \tan^{-1} 2\pi CRF_1}.$$

Appendix 2.

Relation between Constant J *as used here and Boltzmann's Constant* K.

Nyquist (Physical Review, July 1928, p. 112, Eqn. 1) gives the relation $E^2 d\nu = 4KTR d\nu$, where $E^2 d\nu$ is the square of the E.M.F. corresponding to a frequency band of width $d\nu$, the quantity expressed by us as $(\Delta E)^2$.

$$E^2 d\nu = (\Delta E)^2 = J^2TR d\nu.$$

$$\therefore \quad 4KTR d\nu = (\Delta E)^2 J_1^2 TR d\nu,$$

where J_1^2 is the numerical value of J^2 expressed in units consistent with K being expressed in ergs per degree. J^2 as usual here is expressed in micro-micro joules per degree, so that $J^2 = 10^5$, $J_1^2 = 10^5 \cdot 4K$.

$$\therefore \quad J = 200\sqrt{10K}.$$

XCIV. *Two-dimensional Periodic Orbits in the Field of a Non-Neutral.* *By* M. A. Higab, *M.Sc., Ph.D., Lecturer in Applied Mathematics in the Egyptian University, Cairo* *.

THE two-dimensional motion of a charged particle in the field of an electric doublet has recently been discussed by Dr. D. Wrinch (Phil. Mag. xliii. pp. 923–1014, 1923). In this discussion the only periodic orbits obtained have been semicircular; otherwise the path has always been non-periodic.

Sir G. Greenhill (Phil. Mag. xliv. pp. 372–376, 1923) has suggested the discussion of possible closed orbits, and it is the object of this paper to establish the existence and study the nature of these orbits.

The equations of motion are as follows. Let $r=\mathrm{OP}$ be the distance of the electron from O the centre of the doublet, and θ the angle which OP makes with the axis of the doublet, then

$$\ddot{r}-r\dot{\theta}^2=-\frac{\mu}{r^2}-2\lambda\cos\theta, \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta})=-\frac{\lambda\sin\theta}{r^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where λ and μ are the doublet strength and central force constant, respectively, both being positive.

Equation (2) gives at once

$$r^4\dot{\theta}^2=\mathrm{A}+2\lambda\cos\theta, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A is a constant.

Two types of motion will be discussed separately, viz.:

(*a*) Circular motion defined by $r=$constant;

(*b*) General motion where all the coordinates vary.

Circular Motion.

Let $r=a$, where a is a constant. Equations (1) and (3) are identical if $\mathrm{A}=\mu a$.

Therefore we get

$$a^4\dot{\theta}^2=\mu a+2\lambda\cos\theta. \quad . \quad . \quad . \quad . \quad . \quad (3')$$

Since the left-hand side of equation (3′) is positive, the

* Communicated by Prof. A. M. Mosharrafa.

right-hand side must also be positive, and the following cases arise :—

(a) $\mu a > 2\lambda$. The electron goes round and round in circles. The time of one complete revolution is given by

$$T = \frac{4a^2}{\sqrt{\mu a + 2\lambda}} F\left(\frac{\pi}{2}, \sqrt{\frac{4\lambda}{\mu a + 2\lambda}}\right).$$

(b) $\mu a = 2\lambda$. The electron takes an infinite time to reach the axis $\theta = +\pi$ or $\theta = -\pi$.

(c) $0 < \mu a < 2\lambda$. The electron oscillates in an arc of a circle whose amplitude is greater than $\pi/2$ and bounded by the lines

$$\theta = \pm\left[\pi - \cos^{-1}\frac{\mu a}{2\lambda}\right].$$

The periodic time is given by

$$T = \frac{4a^2}{\sqrt{\lambda}} F\left(\frac{\pi}{2}, \sqrt{\frac{\mu a + 2\lambda}{4\lambda}}\right).$$

(d) $\mu = 0$. The electron oscillates in a semicircle between the lines $\theta = \pm\pi/2$. The periodic time is given by

$$T = \frac{4a^2}{\sqrt{\lambda}} F\left(\frac{\pi}{2}, \frac{1}{\sqrt{2}}\right).$$

This is the case discussed by Dr. D. Wrinch.

General Motion.

Since the left-hand side of equation (3) is positive, the right-hand side must also be positive. Therefore A cannot be less than -2λ, and the following cases arise :—

(a) $A > 2\lambda$. In this case $A + 2\lambda\cos\theta$ is always positive, and the motion is not restricted as regards θ. Also the transverse velocity of the electron does not vanish in the finite part of the plane.

(b) $A = 2\lambda$. Here the lines $\theta = \pm\pi$ cannot be crossed.

(c) $0 < A < 2\lambda$. The lines $\theta = \pm\left[\pi - \cos^{-1}\frac{A}{2\lambda}\right]$ cannot be crossed. The angle which defines the region of motion in this case is twice an obtuse angle.

(d) $A = 0$. The lines $\theta = \pm\pi/2$ cannot be crossed.

(e) $0 > A > -2\lambda$. The lines $\theta = \pm \cos^{-1}\frac{|A|}{2\lambda}$ cannot be crossed. The angle which defines the region of motion in this case is twice an acute angle.

(f) $A = -2\lambda$. The motion is along the axis $\theta = 0$.

N.B.—The only cases which give rise to periodic orbits are (a) and (c), so we shall be concerned with their discussion only. In every other case the path is non-periodic.

The Differential Equation of the Path.

Eliminating $\dot{\theta}$ between equations (1) and (3), we get:

$$\ddot{r} = -\frac{\mu}{r^2} + \frac{A}{r^3},$$

the first integral of which is

$$\dot{r}^2 = \frac{2\mu}{r} - \frac{A}{r^2} + B,$$

where B is a constant.

If we put $u = \frac{1}{r}$ and write $\frac{du}{d\theta} = u_1$, we obtain for the differential equation of the path:

$$(A + 2\lambda\cos\theta)u_1^2 = 2\mu u - Au^2 + B, \quad . \quad . \quad . \quad (4)$$

where $(A + 2\lambda\cos\theta)$ is necessarily positive.

Case (a).

$A > 2\lambda$. In equation (4), since $A \neq 0$, we can divide by it and get

$$\left(1 + \frac{2\lambda}{A}\cos\theta\right)u_1^2 = \frac{e^2}{l^2} - \left(u - \frac{1}{l}\right)^2, \quad . \quad . \quad . \quad (5)$$

where

$$\frac{B}{A} + \frac{\mu^2}{A^2} = \frac{e^2}{l^2} \quad \text{and} \quad \frac{\mu}{A} = \frac{1}{l}.$$

Now

$$u_1 = 0 \quad \text{at} \quad u = \frac{1 \pm e}{l}.$$

Three different cases arise:—

(1) $e < 1$. In this case r oscillates between the maximum

and minimum values $\frac{l}{1-e}$ and $\frac{l}{1+e}$ respectively, and the motion is included between the two circles

$$r=\frac{l}{1-e} \quad \text{and} \quad r=\frac{l}{1+e}.$$

The radial velocity vanishes on each of these two circles.

Integrating equation (5) we obtain for the equation of the path

$$\frac{l}{r}=1+e\cos\left[c+2\sqrt{\frac{A}{A+2\lambda}}\,F\left(\psi,\sqrt{\frac{4\lambda}{A+2\lambda}}\right)\right], \quad (6)$$

where c is a constant and $\psi=2\theta$.

For different values of the constant (c) and the modulus $\sqrt{\frac{4\lambda}{A+2\lambda}}$, equation (6) represents a series of curves which may or may not be periodic.

The condition for periodicity is

$$\int_0^{k\pi}\frac{d\psi}{(1-x\sin^2\psi)^{1/2}}=m\pi\sqrt{\frac{2}{2-x}}, \quad . \quad . \quad (7)$$

where

$$x=\frac{4\lambda}{A+2\lambda},$$

and k and m are positive integers.

Corresponding to each pair of positive integers (k, m), a definite value of x may be obtained such as to satisfy equation (7), and the three parameters (k, m, x) will then define a type of periodic orbit. We shall find it convenient to speak of types of class $(m-k+1)$ and order k. In all orbits of order k the motion is represented at $\psi=k\pi$. In this paper typical solutions of equation (7) for pairs of integers have been obtained graphically; the following results have been obtained :—

Types of the First Order, $k=1$.

Orbits of class (1) are given by

$$m=1, \quad x=0, \quad \lambda=0.$$

All orbits of this type are ellipses.

Orbits of class (2) are given by

$$m=2, \quad x=\cdot 998, \quad \frac{A}{\lambda}=2\cdot 007.$$

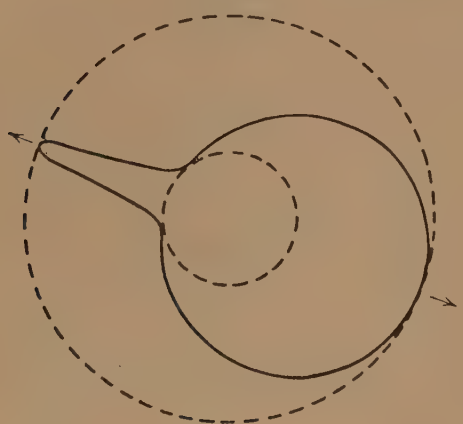
Orbits of this type touch the two circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$ in four points.

Orbits of class (3) are given by

$$m=3, \quad x=\cdot 9999, \quad \frac{A}{\lambda}=2\cdot 0004.$$

Orbits of this type touch the two circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$ in six points.

Fig. 1.



In general, types of order (I.) and class S are given by $m=S$, and the number of points of tangency to the circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$ is 2S.

Theoretically speaking, there are an infinite number of orbits in this class, but as A gets nearer and nearer to 2λ, the electron oscillates closer and closer to the axis $\theta=\pi$.

A typical orbit of class (1) and order (I.) is shown in fig. 1.

Types of the Second Order, $k=2$.

Orbits of class (1) are given by

$$m=2.$$

These orbits are of class (1) and order (I.) described twice.

Orbits of class (2) are given by

$$m = 3, \quad x = \cdot 9781, \quad \frac{A}{\lambda} = 2\cdot 08966.$$

Orbits of this type touch the two circles $r = \frac{l}{1-e}$ and $r = \frac{l}{1+e}$ in six points.

Orbits of class (3) are given by

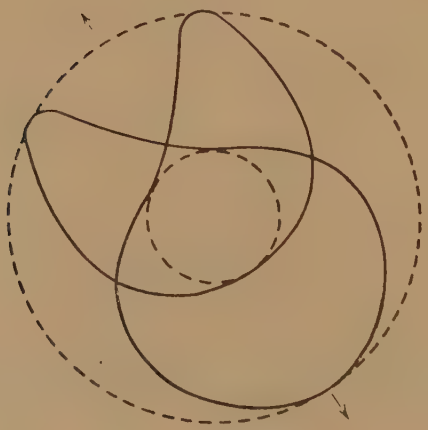
$$m = 4.$$

These orbits are of class (2) and order (I.) described twice.

Orbits of class (4) are given by

$$m = 5, \quad x = \cdot 9998, \quad \frac{A}{\lambda} = 2\cdot 0019.$$

Fig. 2.



Orbits of this type touch the two circles $r = \frac{l}{1-e}$ and $r = \frac{l}{1+e}$ in ten points.

In general, types of order (II.) and class S are given by $m = S+1$. If $S+1$ is even, this orbit is that of class $\left(\frac{S+1}{2}\right)$ of the first order described twice; but if $S+1$ is odd, then this is the S periodic of the second order, and the number of points of tangency to the two circles is $2S+2$.

A typical orbit of class (2) and order (II.) is shown in fig. 2.

Generally the periodic orbits of order t and class S are given by $k=t$, $m=S+t-1$, x being a root of the equation

$$tF\left(\frac{\pi}{2},\ \sqrt{x}\right)=\frac{m\pi}{2}\sqrt{\frac{2}{2-x}}.$$

If m and t are not prime to one another, then these orbits will be orbits of a lower order multiply described.

(2) $e=1$. The outer circle becomes infinite, and r passes through the minimum value $l/2$ and extends to infinity. Thus the motion is outside the circle $r=l/2$. The path in this case touches the circle at infinity.

(3) $e>1$. The outer circle does not exist, and r passes through the minimum value $\frac{l}{1+e}$. Thus the motion is outside the circle $r=\frac{l}{1+e}$. The path in this case proceeds to infinity along asymptotes.

Case (c).

$0<A<2\lambda$. The differential equation of the path is

$$\left(1+\frac{2\lambda}{A}\cos\theta\right)u_1^2=\frac{e^2}{l^2}-\left(u-\frac{1}{l}\right)^2, \quad . \quad . \quad . \quad (8)$$

where

$$\frac{B}{A}+\frac{\mu^2}{A^2}=\frac{e^2}{l^2} \quad \text{and} \quad \frac{\mu}{A}=\frac{1}{l}.$$

Now

$$u_1=0 \quad \text{at} \quad u=\frac{1\pm e}{l}.$$

Three different cases arise :—

(1) $e<1$. In this case r oscillates between the maximum and minimum values $\frac{l}{1-e}$ and $\frac{l}{1+e}$ respectively, and the motion is included between the two circles $r=\frac{l}{1-e}$ and $r=\frac{l}{1+e}$. Integrating equation (8) we get the equation of the path to be

$$\frac{l}{r}=1+e\cos\left[c+\sqrt{\frac{A}{\lambda}}F\left(\psi,\ \sqrt{\frac{A+2\lambda}{4\lambda}}\right)\right. . \quad (9)$$

For different values of the constant c and the modulus $\sqrt{\frac{A+2\lambda}{4\lambda}}$, equation (9) represents a series of curves which may or may not be periodic.

The condition for periodicity is

$$\int_0^{k\pi} \frac{d\psi}{(1-x\sin^2\psi)^{1/2}} = \frac{2m\pi}{\sqrt{4x-2}}, \quad . \quad . \quad . \quad (10)$$

where $$x = \frac{A+2\lambda}{4\lambda}$$

and $$\psi = \sin^{-1}\left[\sqrt{\frac{A+2\lambda}{4\lambda}}\sin\frac{\theta}{2}\right],$$

and k and m are positive integers.

Equation (10) has been solved graphically and the following results obtained :—

Types of Order (I.), $k=1$.

Orbits of class (1) are given by

$$m = 1, \quad x = \cdot 8851, \quad \frac{A}{\lambda} = 1\cdot 5404.$$

Orbits of this type touch the circles $r = \frac{l}{1-e}$ and $r = \frac{l}{1+e}$ in three points.

Orbits of class (2) are given by

$$m = 2, \quad x = \cdot 999, \quad \frac{A}{\lambda} = 1\cdot 99.$$

Orbits of this type touch the circles $r = \frac{l}{1-e}$ and $r = \frac{l}{1+e}$ in five points.

Theoretically speaking, there are an infinite number of orbits of this order, but as A gets nearer to 2λ, the electron oscillates nearer the axis $\theta = \pi$.

A typical orbit of class (1) and order (I.) is shown in fig. 3.

Types of Order (II.), $k=2$.

Orbits of class (1) are given by

$$m = 1, \quad x = \cdot 6411, \quad \frac{A}{\lambda} = \cdot 5644.$$

Orbits of this type touch the circles $r = \frac{l}{1-e}$ and $r = \frac{l}{1+e}$ in two points.

Orbits of class (2) are given by

$$m = 2.$$

These are the orbits of class (1) and order (I.) described twice.

Orbits of class (3) are given by

$$m = 3, \quad x = \cdot 9807, \quad \frac{A}{\lambda} = 1 \cdot 9228\,\lambda.$$

Fig. 3.

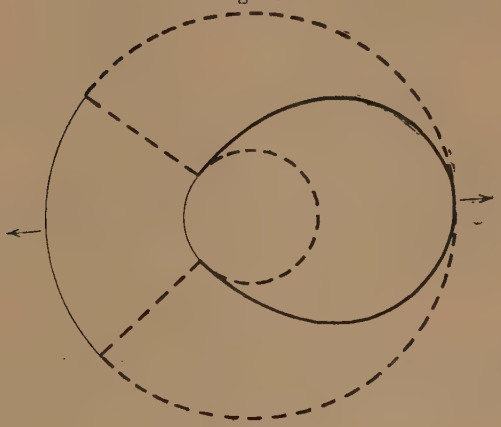
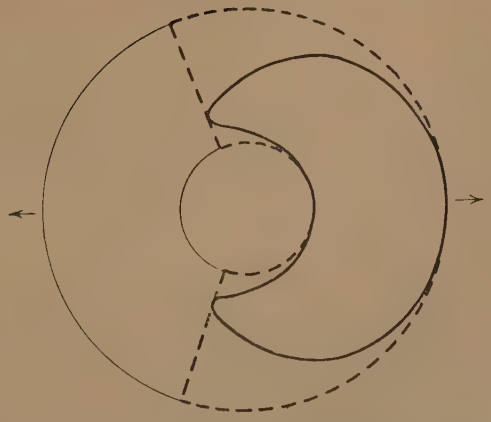


Fig. 4



Orbits of this type touch the circles $r = \frac{l}{1-e}$ and $r = \frac{l}{1+e}$ in six points.

As before, there are an infinite number of orbits of this order.

A typical orbit of class (1) and order (II.) is shown in fig. 4.

Generally the periodic orbits of order t and class S are defined by $k=t$, $m=\mathrm{S}$, x being a root of the equation

$$t\mathrm{F}\left(\frac{\pi}{2},\ \sqrt{x}\right)=\frac{m\pi}{\sqrt{4x-2}}.$$

If m and t are not prime to one another, then these orbits will be orbits of lower order multiply described.

(2) $e=1$. The path is always open and touches the circle at infinity.

(3) $e>1$. The path is always open and proceeds to infinity along asymptotes.

In conclusion, I wish to express my thanks to Prof. S. Brodetsky, of Leeds University, under whose supervision the above work has been done, and to Prof. A. M. Mosharrafa for criticisms and suggestions.

Summary.

The motion of a charged particle in the field of an electric doublet is discussed.

Conditions for periodic orbits are obtained, and typical examples are discussed and illustrated.

XCV. *Application of Talbot's Law to Photoelectric Cells with a Non-linear Illumination-current Characteristic.* *By* G. H. Carruthers, *B.Sc.*, *A.R.C.S.* (*Admiralty Research Laboratory*), *and* T. H. Harrison, *Ph.D.*, *B.Sc.*, *A.Inst.P.* (*National Physical Laboratory*)*.

Abstract.

A simple analysis shows that Talbot's law should be valid for a cell in which the photo-electric current is proportional to the illumination, but should fail for a cell in which this proportionality does not hold. A series of careful experiments with cells for which this proportionality holds, and with others for which the proportionality fails, shows, however, that Talbot's law holds for both types.

From this is deduced an explanation as to the cause of this failure of proportionality, based on a rapid fatigue effect during the time that the cell is exposed to the illumination,

* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

and a recovery effect during the period that the cell is occulted by the sector. With a cell for which the proportionality law holds there is no such rapid fatigue and recovery.

TALBOT'S law is stated by Helmholtz as follows :—

"If any part of the retina is excited with intermittent light, recurring periodically and regularly in the same way, and if the period is sufficiently short, a continuous impression will result which is the same as that which would result if the total light received during each period were uniformly distributed throughout the whole period *."

Normally a sector disk rotating about its centre is employed to obtain the intermittent effect, and in this case Talbot's law reduces to the statement that the effective brightness of the source is proportional to the angular opening of the sector.

E. P. Hyde, who conducted a searching test of Talbot's law as applied to the eye, said that "Talbot's law is thus a statement of physiological rather than physical phenomena, and depends for its explanation on the action of the eye †.

The results of Hyde's investigations established the accuracy of Talbot's law applied to the eye with an accuracy of 0·3, which represented the limit of accuracy of experiment.

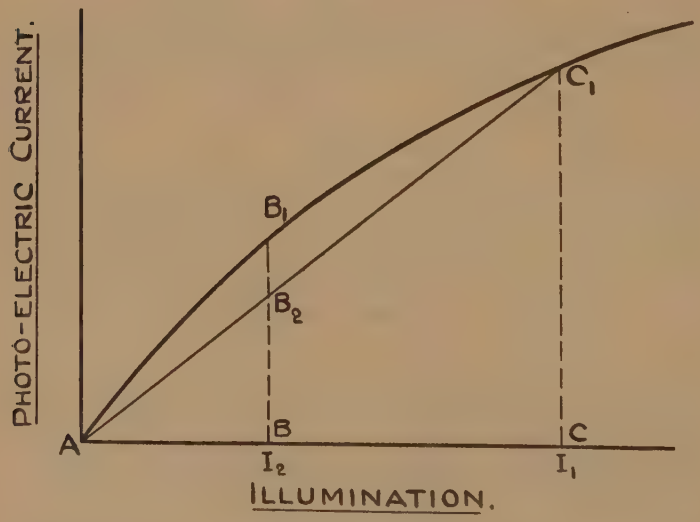
The applicability of Talbot's law to the bolometer was tested by W. W. Coblenz ‡, who found that the energy transmitted by a rotating sector disk is appreciably greater than the theoretical value. The experimental evidence showed that this increase varied with the speed of the disk and with the distance between the sector disk and the bolometer. No completely satisfactory explanation was offered for this failure of Talbot's law, but it was considered probably due to diffraction of the waves of longer wavelength.

The applicability of Talbot's law to the photoelectric cell has been tested by J. Kunz § and by H. E. Ives Dushman and Karrer ‖. In the work of Kunz the investigation was confined to one photoelectric cell for which the photoelectric current was proportional to the illumination, that is, it

* *Physiolog Optik*, iii. Auflage, ii. p. 174.
† Bulletin of the Bureau of Standards, ii. p. 1 (1906).
‡ Bulletin of the Bureau of Standards, iv, p. 455 (1907).
§ Astrophysical Journal, xlv. pp. 76–77 (1917).
‖ Astrophysical Journal, xliii. pp. 1–35 (1916).

possessed a linear illumination-current characteristic. The characteristic was found by varying the illumination on the cell firstly by means of crossed Nicol prisms, and secondly by means of a rotating disk with various angular apertures. Both methods of varying the illumination gave straight lines, with the same slope in each case, and from this Kunz concluded that Talbot's law holds for the photoelectric cell. Unfortunately no numerical data are given from which the accuracy of the agreement of the two methods can be obtained. Also the fact that the one cell tested, on which his conclusion is based, possessed a linear illumination-current

Fig. 1.



characteristic is distinctly unfortunate, as will be seen by consideration of the following.

Consider a cell with a non-linear illumination-current characteristic, which is shown in fig. 1. When this cell is exposed to a steady illumination I_1, the photoelectric current is represented by CC_1. If the cell is exposed to steady illumination I_2, then the photoelectric current will be BB_1. Let us now consider the case in which the illumination I_1 is reduced to the value I_2 by the introduction of a sector disk of ratio I_2/I_1 ; then according to the usual conception of the photoelectric current by which the passage of electrons occurs almost instantaneously on exposure to light, it is reasonable to suppose that the photoelectric current CC_1

will be reduced not to the value of BB_1, but to BB_2, where B_2 lies on the straight line joining the origin to C_1, since the electrons now pass only for periods totalling I_2/I_1 per unit time. Thus, whatever the true characteristic of the cell may be, a straight-line relation will be obtained by varying the angular opening of the sector disk.

It is evident from this that the investigation of Kunz using a linear cell is by no means conclusive evidence of the validity of Talbot's law as applied to photoelectric cells in general. The same objection applies to the work of Ives, who also tested the law on a cell with a linear characteristic. Ives, however, went one step further by checking one point on the characteristic curve of a cell with a non-linear relationship. From this he also concludes that Talbot's law can be applied to photoelectric cells. No data from which conclusions can be drawn as to the amount of departure from linearity of the cell, the closeness of the agreement between the two methods, or the experimental error are given. In addition to the above investigations, an earlier test was carried out by Elster and Geitel; here again tests were carried out on cells with a linear characteristic.

In view of the unsatisfactory nature of the evidence of the applicability of Talbot's law to photoelectric cells, particularly to those with non-linear characteristics, it was decided to carry out a thorough investigation, and for this purpose specimens representing as many different types of cells as possible were collected. The collection included cells made with potassium, sodium, rubidium, cæsium, and lithium. Some were gas-filled, others were evacuated.

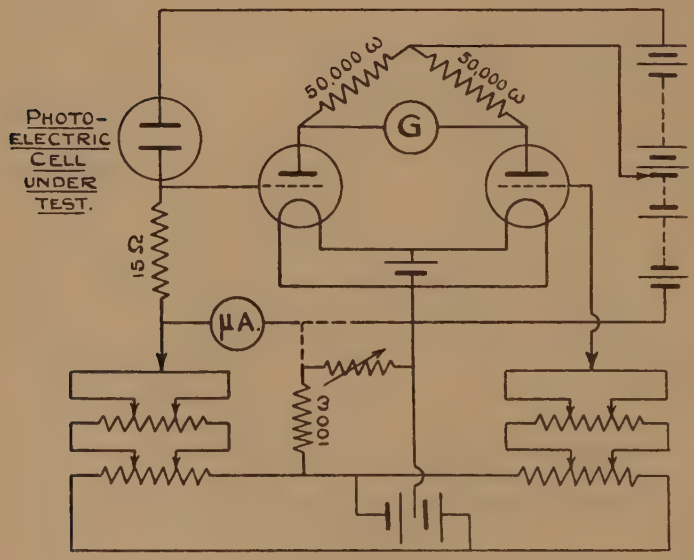
Preliminary experiments were tried with a Lindemann electrometer with a view to measuring the potential of the junction-point of a cell in series with a high resistance. On account, however, of a small creep in the deflexion of the needle when a constant potential was applied, it was found impossible to take observations of sufficient accuracy. Recourse was then had to an apparatus that had been previously designed by one of the authors for photometric work on principles outlined by C. H. Sharp and H. A. Smith *.

The arrangement of the apparatus is shown in fig. 2. The cathode of the cell to be tested is connected in series with a 15-megohm resistance, and the junction-point to the grid of a thermionic valve. The other end of the 15-megohm

* C. H. Sharp and H. A. Smith, Trans. Ill. Eng. Society, p. 431 (New York, 23 April, 1928).

resistance is connected to the slider of a potential dividing system so that the grid of the left-hand valve can be set at any desired potential within a range of +2 volts relative to the negative end of its filament. The grid of the right-hand valve is connected directly to the slider of another similar potential divider (lower right-hand corner of the diagram). Initially the photoelectric cell is in darkness, and there is only the dark current passing through the 15-megohm leak. The grid of the left-hand valve is set at zero voltage relative

Fig. 2.



to the negative end of the filament, as indicated by the microammeter, whilst that of the right-hand valve is set at such a potential that the Wheatstone bridge formed by the two valves and the two 50,000-ohm resistance is balanced, and no current passes through the galvanometer G. If, now, the photoelectric cell is illuminated so that there is an increase in the current, the grid of the left-hand valve acquires a positive potential, and the bridge is put out of balance. The balance, however, can be restored by moving the sliders of the left-hand potential divider to which the 15-megohm leak is connected. When this is done, the grid of the left-hand valve is again at zero potential, and the

microammeter, which is used as a millivoltmeter, gives a reading corresponding to the fall in potential along the grid-leak due to the photoelectric current passing through it. In this way the reading on the microammeter is directly proportional to the photoelectric current. In order to increase the range of the microammeter, another potential dividing system is used in connexion with a switch by which it is either inserted or cut out of action. No trouble was experienced through unsteadiness of the valves, but electrostatic shielding, obtained by placing all the apparatus inside an earthed metal-lined box, was essential. The photoelectric cell, behind a suitably-screened aperture in the side of the box, was exposed to the light from a 1000-watt concentrated uniplanar filament lamp mounted on a photometer bench. The size of the filament was 1·5 cm. by 1·3 cm., and the correction for size of filament was found to be negligible. To ensure that the voltage across the lamp was constant, a potentiometer was employed.

The sectors used in conjunction with the thermionic bridge were made with two equal apertures symmetrically arranged. They were carefully cut out of millboard, the centres being strengthened with brass centre-pieces which closely fitted a sleeve fixed to the shaft of a small motor. The latter, which was mounted on a separate support to avoid vibration troubles, was arranged so that the sectors were about 10 cm. in front of the cell. To test whether the response of the system was affected by any sparking from the motor, the latter was run without a sector disk, and it was found that the balance of the bridge was in no way disturbed. Each sector was calibrated, the ratio of the open to the closed part being determined to five in the fourth place of decimals. The nominal values of the ratios of the sectors were 0·75, 0·667, 0·5, 0·333, 0·25, 0·167, and the actual values agreed with these to one in the third place of decimals.

The results of the tests on six cells are given in the paper. The first set of results refers to a potassium neon cell with a wire ring anode which had been sensitized by the Elster and Geitel process. The inside of the cell was, except for the window, completely covered with the alkali metal, as is the usual practice. This cell showed a decided departure from linearity in its illumination-current characteristic, that is to say, the photoelectric current was not proportional to the illumination when this was varied by moving a lamp along a photometer bench and applying the inverse square laws. The second set of results refers to a cæsium vacuum cell with a wire ring anode, which also showed a decided departure

from linearity, but its response to a given illumination was apt to vary slightly. This was probably caused by the shortness of the glass neck which separated the anode and cathode, and resulted in a dark current of slightly variable magnitude. The third set of results refers to a rubidium helium cell with a wire ring anode. With this cell, as with the cæsium cell, there was an appreciable dark current when 100 volts were applied. The fourth set of results refers to a sodium vacuum cell provided with a quartz window for use in the ultra-violet. The anode again consisted of a wire ring. Both the rubidium helium and the sodium vacuum cells show a slight departure from linearity. The fifth set of results refers to a rubidium vacuum cell. In this cell the alkali metal cathode, instead of being on the inside glass surface, as is usual, was formed on a metallic plate. The silvered inner surface of the cell formed the anode. The sixth set of results refers to a potassium neon cell made of uviol glass. In order to secure a uniform field, the anode of this cell is in the form of a grid. The two cells last mentioned showed no departure from linearity greater than that which could bo safely attributed to experimental error. Other cells were tested, in particular a lithium cell provided with a quartz window. This cell, however, which was designed for use in the ultra-violet, was so very insensitive, even to light from a quartz mercury vapour lamp, that no useful results could be obtained. This insensitivity may have been due to faulty manufacture. Three other cells were tested and, being linear, gave no additional information, and the results are not included.

In taking observations the routine adopted was first to observe the photoelectric current when the cell was exposed to a given illumination. The illumination was then reduced in a given ratio, firstly by introducing a sector disk, and secondly by moving the lamp along the photometer bench to the appropriate distance, as given by the inverse square law. Finally, as a check, and to eliminate any slow changes, the sector disk was again used, and also there was again an exposure to the full steady illumination. Between each of these operations a rebalancing of the bridge was made in case of any alteration of the zero. In order to avoid any slow changes in the response of the cell, the precaution was taken of not exposing the cell unnecessarily. With regard to the potassium cell—the first cell mentioned—an attempt was made to increase the non-linearity by raising the voltage and also the illumination. This, as was feared, resulted in arcing the cell, the inside of which seemed to be filled with

a reddish glow similar to that observed in neon lamps. A subsequent determination of its illumination-current characteristic showed it to be completely changed. It was now quite linear and four times as sensitive, this increase being chiefly in the blue region. A redetermination of its characteristic six weeks later showed, however, that the cell was gradually reverting to its previous state. This may be a point of further interest in the determination of the reason of non-linearity. The results obtained immediately after the arcing of the cell are also given below.

The results obtained with the thermionic-bridge system are given in Tables I.–VII. They show that the probable error in the determination of the ratios of the photoelectric currents is 2×10^{-3}. Apart from the cæsium cell, the greatest difference shown by any of the cells tested between the inverse square result and the sector disk result was three times the probable error. It is to be concluded from the experimental results with the thermionic-bridge system that, contrary to expectation, Talbot's law holds for photoelectric cells whether their response is proportional to the illumination or not.

TABLE I.—Thermionic Bridge.

Potassium neon cell.

Diameter of window, 18 mm.

100 volts across cell.

Lamp at 60 volts, giving 490 candle-power.

Current flowing through cell for maximum illumination (605 metre candles) was $4{\cdot}0 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·764	0·687	0·523	0·356	0·271	0·184	0·093
Departure from linearity $\times 10^3$.	+14	+20	+23	+23	+21	+17	+10
Current ratio (sector disk).	0·766	0·683	0·527	0·355	0·270	0·183	
Departure from linearity $\times 10^3$.	+16	+16	+27	+22	+20	+16	
Inverse square less sector ratio $\times 10^3$.	− 2	+ 4	+ 4	+ 1	+ 1	+ 1	

TABLE II.—Thermionic Bridge.

Cæsium vacuum cell.

Diameter of window, 20 mm.

100 volts across cell.

Lamp run at 55 volts, giving 350 candle-power.

Current flowing through cell for maximum illumination (432 metre candles) was $3{\cdot}4 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·765	0·691	0·521	0·361	0·272	0·188	0·100
Departure from linearity $\times 10^3$.	+15	+24	+21	+28	+22	+21	+17
Current ratio (sector disk).	0·761	0·682	0·521	0·362	0·280	0·191	
Departure from linearity $\times 10^3$.	+11	+15	+21	+29	+30	+24	
Inverse square less sector ratio $\times 10^3$.	+ 4	+ 9	0	− 1	− 8	− 3	

TABLE II *a*.—Galvanometer.

Cæsium vacuum cell.

Lamp at 77 volts, giving 1149 candle-power.

Current flowing through cell for maximum illumination (1418 metre candles) was 11×10^{-8} amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·750	0·683	0·519	0·352	0·269	0·182	0·097
Departure from linearity $\times 10^3$.	0	+16	+19	+19	+19	+15	+14
Current ratio (sector disk).	0·755	0·680	0·516	0·350	0·272	0·185	
Departure from linearity $\times 10^3$.	+5	+13	+16	+17	+22	+18	
Inverse square less sector ratio $\times 10^3$.	−5	+ 3	+ 3	+ 2	− 3	− 3	

TABLE III.—Thermionic Bridge.

Rubidium helium cell.

Diameter of window, 20 mm.

100 volts across cell.

Lamp run at 42 volts, giving 124 candle-power.

Current flowing through cell for maximum illumination (153 metre candles) was $4{\cdot}6 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·125
Current ratio (inverse square law).	0·757	0·670	0·507	0·340	0·255	0·174	0·129
Departure from linearity $\times 10^3$.	+7	+3	+7	+7	+5	+7	+4
Current ratio (sector disk).	0·753	0·672	0·510	0·340	0·258	0·173	
Departure from linearity $\times 10^3$.	+3	+5	+10	+7	+8	+6	
Inverse square less sector ratio $\times 10^3$.	+4	−2	−3	0	−3	+1	

TABLE IV.—Thermionic Bridge.

Sodium vacuum cell with quartz window.

Diameter of window, 18 mm.

100 volts across cell.

Lamp run at 60 volts, giving 490 candle-power.

Current flowing through cell for maximum illumination (605 metre candles) was $3{\cdot}4 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·756	0·670	0·505	0·341	0·257	0·172	0·087
Departure from linearity $\times 10^3$.	+6	+3	+5	+8	+7	+5	+4
Current ratio (sector disk).	0·755	0·669	0·505	0·340	0·257	0·173	
Departure from linearity $\times 10^3$.	+5	+2	+5	+7	+7	+6	
Inverse square less sector ratio $\times 10^3$.	+1	+1	0	+1	0	−1	

TABLE V.—Thermionic Bridge.

Rubidium vacuum cell, plate type.

Diameter of window, 20 mm.

100 volts across cell.

Lamp run at 47 volts, giving 194 candle-power.

Current flowing through cell for maximum illumination (240 metre candles) was $4{\cdot}3 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·749	0·666	0·503	0·337	0·254	0·168	0·085
Departure from linearity $\times 10^3$.	−1	−1	+3	+4	+4	+1	+2
Current ratio (sector disk).	0·747	0·666	0·498	0·333	0·253	0·162	
Departure from linearity $\times 10^3$.	−3	−1	−2	0	+3	−5	
Inverse square less sector rati $\times 10^3$.	+2	0	+5	+4	+1	+6	

TABLE V*a*.—Galvanometer.

Rubidium vacuum cell, plate type.

Lamp run at 71·0 volts, giving 890 candle-power.

Current flowing through cell for maximum illumination (1099 metre candles) was 19×10^{-8} amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·749	0·669	0·409	0·330	0·246	0·165	0·081
Departure from linearity $\times 10^3$.	−1	+2	−1	+3	−4	−2	−2
Current ratio (sector disk).	0·746	0·674	0·496	0·328	0·247	0·164	
Departure from linearity $\times 10^3$.	−4	+7	−4	−5	−3	−3	
Inverse square less sector ratio $\times 10^3$.	+3	−5	+3	+2	−1	+1	

TABLE VI.—Thermionic Bridge.

Potassium neon cell made of uviol glass.

Anode of cell in grid form.

Diameter of cell window, 20 mm.

90 volts across cell.

Lamp run at 42 volts, giving 124 candle-power.

Current flowing through cell for maximum illumination (153 metre candles) was $4{\cdot}2 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0 167	0·083
Current ratio (inverse square law).	0·752	0·668	0·504	0·334	0·251	0·167	0·083
Departure from linearity $\times 10^3$.	+2	+1	+4	+1	+1	0	0
Current ratio (sector disk).	0·750	0·668	0·500	0·330	0·251	0·166	
Departure from linearity $\times 10^3$.	0	+1	0	−3	+1	−1	
Inverse square less sector ratio $\times 10^3$.	+2	0	+4	+4	0	+1	

TABLE VII.—Thermionic Bridge.

Potassium neon immediately after arcing.

Lamp at 42 volts, giving 124 candle-power.

Current flowing through cell for maximum illumination (153 metre candles) was $4{\cdot}7 \times 10^{-8}$ amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·755	0·668	0·502	0·336	0·253	0·168	0·085
Departure from linearity $\times 10^3$.	+5	+1	+2	+3	+3	+1	+2
Current ratio (sector disk).	·751	·667	0·500	0·333	0·253	0·166	
Departure from linearity $\times 10^3$.	+1	0	0	0	+3	−1	
Inverse square less sector ratio $\times 10^3$.	+4	+1	+2	+3	0	+2	

TABLE VII *a*.—Galvanometer.

Potassium neon after arcing.

Lamp at 55·6 volts, giving 367 candle-power.

Current flowing through cell for maximum illumination (453 metre candles) was 18×10^{-8} amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·751	0·668	0·499	0·326	0·247	0·161	0·083
Departure from linearity $\times 10^3$.	+1	+1	−1	−7	−3	−6	0
Current ratio (sector disk).	0·748	0·666	0·499	0·325	0·247	0·161	
Departure from linearity $\times 10^3$.	−2	−1	−1	−8	−3	−6	
Inverse square less sector ratio $\times 10^3$.	+3	+2	0	+1	0	0	

TABLE VII *b*.—Galvanometer with Shunt.

Potassium neon after arcing.

Lamp at 77 volts, giving 1149 candle-power.

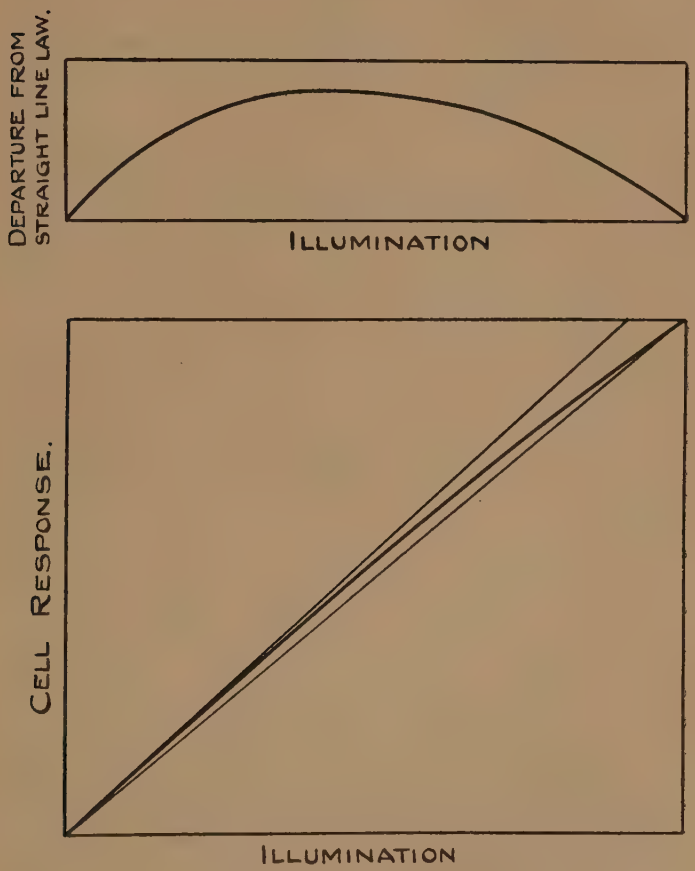
Current flowing through cell for maximum illumination (1418 metre candles) was 84×10^{-8} amp.

Ratio of reduced illumination to maximum illumination.	0·750	0·667	0·500	0·333	0·250	0·167	0·083
Current ratio (inverse square law).	0·747	0·665	0·498	0·328	0·248	0·163	0·080
Departure from linearity $\times 10^3$.	−3	−2	−2	−5	−2	−4	−3
Current ratio (sector disk).	0·749	0·669	0·500	0·331	0·250	0·164	
Departure from linearity $\times 10^3$.	−1	+2	0	−2	0	−3	
Inverse square less sector ratio $\times 10^3$.	−2	−4	−2	−3	−2	−1	

In the lower part of fig. 3 the illumination-current curve of the potassium neon cell before the glow discharge occurred is shown. The ordinates represent the photoelectric current

and the abscissæ the illumination. The straight line connecting the origin with the point on the curve corresponding to the maximum illumination represents the response which, according to the argument already outlined, would be given by the cell when the illumination is varied by means of the

Fig. 3.



sector. The upper part of fig. 3 represents on a large scale the difference between this straight line and the actual illumination-current curve which, since Talbot's law is obeyed, was found to be the same when the illumination was varied with sector disks as when it was varied by altering the distance of the lamp. There is also shown the tangent of the curve at the origin ; this will be referred to later.

The curves for the other cells are not included, as they give no additional information.

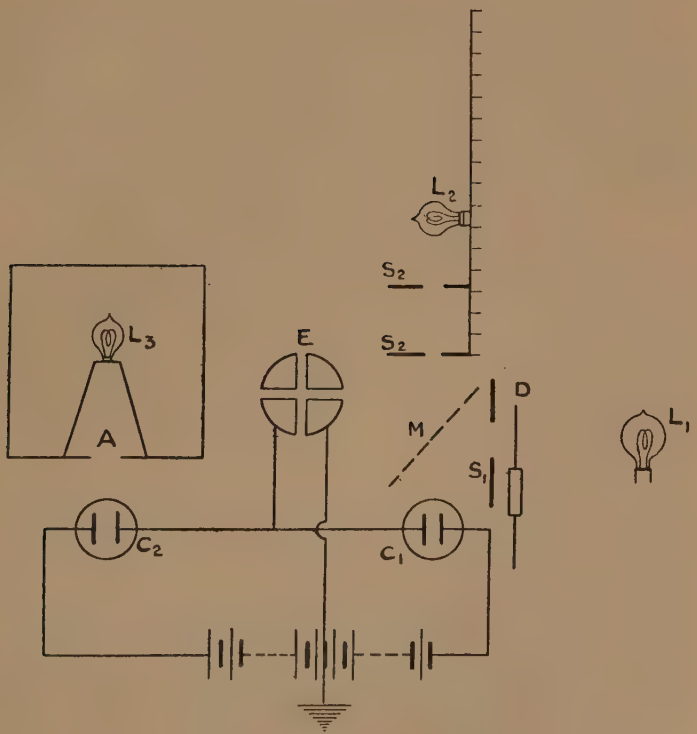
Part of the routine test on each cell was the variation of the sector-speed over a range from about five revolutions to fifty revolutions per second. The balance of the bridge was quite unaltered by those changes of sector-speed, and this showed not only that any changes of the average response of the cell were smaller than could be detected with the apparatus, but also that the intermittent photoelectric current through the cell was being correctly integrated by the apparatus. If, for instance, such a strong illumination were employed that the change of potential at the junction of the cell and the 15-megohm resistance was so great that when applied to the grid of the valve the latter was no longer working on the straight-line portion of its characteristic, then this would be indicated by an apparent change of photoelectric current with change of sector-speed. Thus, when using intermittent illumination, there is an upper limit to the brightness of the source that may be used in conjunction with the thermionic bridge, so that in order to test the validity of Talbot's law over a wider range a simple galvanometer circuit was employed. These results are given in Tables II *a*, V *a*, VII *a*, and VII *b*, and confirm, within experimental error, those obtained with the thermionic bridge, showing that Talbot's law holds even for the highest illuminations. One thing that came out clearly in this work was that cells of the short-necked type have a very large undesirable dark current which varies from day to day. The cæsium cell was a typical example of this.

In order to investigate the validity of Talbot's law with a higher degree of precision than was obtainable using the thermionic bridge, further experiments were conducted with an apparatus which has been described in detail elsewhere*. It will be sufficient to give here a brief outline of the essential features, which are shown diagrammatically in fig. 4. Two photoelectric cells, C_1, the one to be tested, and any second cell, C_2, are connected in series with a 200-volt battery, the centre-point of which is earthed. The junction-point of the cells is connected to one pair of quadrants of a Compton electrometer E, the other pair being earthed. M is a sliding mirror by which C_1 can be illuminated either by the lamp L_1, which is fixed in position, or by the lamp L_2, which can be moved along a photometer-bench. C_2 is illuminated by a source which can be kept constant at any

* T. H. Harrison, Proc. Opt. Convention, 1926, p. 245.

required value. In this case it conveniently took the form of a lamp L_3, placed in a 4-ft. cube, this being already in position in connexion with other work. Between the lamp L_1 and the mirror M a sector could be rotated, and thus reduce the effective illumination from L_1. The procedure adopted in the test was to illuminate C_1 by L_1 and C_2 by L_3, adjusting the voltage across L_3 until the photoelectric current

Fig. 4.



in C_2 was equal to that in C_1. When this adjustment was made the junction-point of the cells remained at earth potential, and the electrometer needle was undeflected. The mirror M was then raised so that C_1 was illuminated by L_2 instead of L_1. The position of L_2 on the bench was then adjusted until the electrometer again showed no deflexion, and the bench-reading noted. As a check that the photoelectric current per unit illumination for both cells had remained

constant over the short time occupied in the last adjustment, the mirror M was lowered again so that C_1 was illuminated by L_1, and an observation was taken to ensure that the system was still balanced. The sector was then set running, thus reducing the effective illumination from L_1, and consequently the photoelectric current through C_1. The photoelectric current through C_2 was now decreased by the same amount by lowering the illumination from L_3 partly by closing the aperture A in the cube and partly by lowering the voltage across L_3, the latter procedure being used as a fine adjustment. When this operation was completed, the electrometer showed no deflexion. Finally, M was raised, thus illuminating C_1 by L_2, the latter being moved along the bench until the balance was restored. With this arrangement any slow changes in the response of the cell are entirely eliminated. In any set of observations it was necessary to keep constant the voltages across L_1 and L_2, and this was

Table VIII.—Electrometer Apparatus.

Inverse square response less sector response $\times 10^4$. for	0·7500	0·5000	0·2500
Potassium neon cell	−14	+ 2	−12
Cæsium vacuum cell	+ 7	−10	− 4
Rubidium helium cell	−12	+ 9	+10
Rubidium vacuum cell, plate type	− 7	+ 5	0
Potassium neon cell made of uviol glass.	+ 5	+ 6	− 9

tested by means of a potentiometer. For this series of tests special sector disks, whose ratios were known accurately to four places of decimals, were employed.

Five cells were tested on this apparatus, the results being given in Table VIII. The same photoelectric current was produced when the illumination was varied either by applying the inverse square law or by interposing a sector disk. The probable experimental error was $\pm 0{\cdot}0007$.

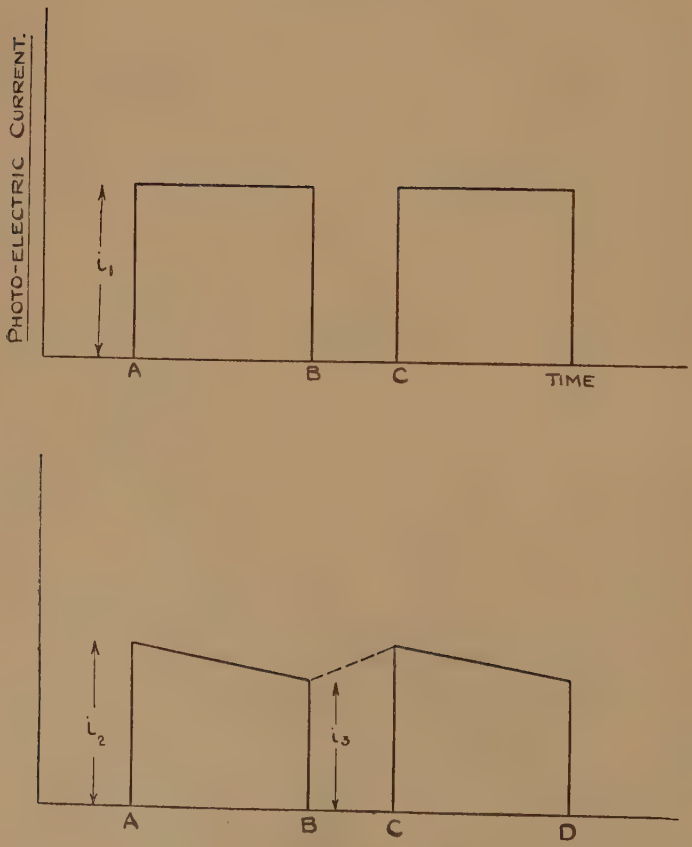
The fact that Talbot's law holds for cells with a non-linear illumination-current relationship indicates a reason for their non-linearity. In the case of a non-linear cell, there are theoretical reasons for believing that the absence of proportionality between illumination and photoelectric current is not due to any intrinsic property of the alkali metal, but to some accidental property of the cell itself, by virtue of which the condition of the cell with regard to its internal electric fields or to gaseous layers is changed upon exposure to illumination. If we suppose this to be the

case, then, if the cause of non-proportionality could be removed, the curves showing the relation between photoelectric current and illumination would become a straight line, which would be the tangent of the origin of the former non-linear curve. The tangent is shown in the lower diagram of fig. 3. It would appear then that if, in an experimental determination of the illumination-current curve of a cell, it were possible to take measurements of photoelectric current immediately after exposure to light, and between each exposure the cell could be obscured for a sufficient length of time for complete recovery from photoelectric fatigue, then the curve obtained would be linear for all cells. In practice, however, measurements can not be made instantaneously, but a lapse of several seconds must take place. With cells in which the proportionality between photoelectric current and illumination holds, the instantaneous reading and the steady reading after a few seconds are the same. For non-proportional cells, however, it would seem that a rapid fatigue occurs, which results after a few seconds in a steady reading of lower value than the instantaneous value. This assumption is supported by the fact that it furnishes an explanation why the departure from linearity of the characteristic is the same for intermittent illumination as for continuous illumination of the same average value. Considering a linear cell in the first place, and neglecting any lag due to resistance and capacity in the circuit, a sector rotating between a light and a photoelectric cell would give a time-current curve as in fig. 5 *a*. A corresponds to a point when the cell is exposed, and the photoelectric current immediately rises to i_1. At B the cell is occulted by the sector, and the current falls to zero again. At C, the cell being again exposed, the current again rises to i_1.

With a non-linear cell in which the current is less than it should be for a strict proportionality, there must be a fatigue during the time that the cell is exposed and a recovery during the time that the cell is occulted by the sector. Thus the current-time curve of such a cell intermittently illuminated after a steady state has been reached would be as shown in fig. 5 *b*. At A the cell is exposed and the photoelectric current rises to a certain value—say i_2. Between A and B the cell is exposed and the current decreases slightly, due to a rapid fatigue, to a value i_3. At B the light is cut off by the sector and the current falls to zero. While the cell is in darkness there is a tendency to recover, and the dotted line represents the potential or virtual response of the cell or the current that would flow through the cell if it

were suddenly exposed at any time between B and C At C the cell is exposed by the sector, and if the steady state has been reached the current again rises to i_2. When the steady state has been reached there is a constant difference between the value of the ordinates at the beginning and end of any exposure, and the response of

Figs. 5 *a* and 5 *b*.



the cell is moving over one small portion of the fatigue curve and one small portion of the recovery curve, and these portions, if the speed of the sector is fast, are to a first approximation straight lines. The portions of the fatigue and recovery curves about which the cell oscillates are, under these conditions, independent of sector speed, being solely determined by the angular opening of the apertures.

If m_F is the slope of the portion of fatigue curve, m_R is the slope of the portion of the recovery curve, n is the number of revolutions per unit, and ω the angular opening in the sector disk, then equating the fatigue over the interval $\frac{1}{n}\frac{\omega}{2\pi}$, during which the cell is exposed to the recovery over the interval $\frac{1}{n}\left(\frac{2\pi-\omega}{2\pi}\right)$, during which the cell is occulted,

$$m_F \cdot \frac{1}{n}\frac{\omega}{2\pi} = m_R \cdot \frac{1}{n}\left(\frac{2\pi-\omega}{2\pi}\right)$$

$$\frac{m_F}{m_R} = \frac{2\pi-\omega}{\omega}.$$

Thus for a sector with angular opening ω the points of the fatigue and recovery curves about which the response of the cell will oscillate are those points where the differential coefficients are m_F and m_R respectively. Furthermore, since Talbot's law is obeyed, the portions of the fatigue and recovery curves traversed by the cell for intermittent illumination must be so situated that the combined fatigue and recovery effects lead to the same value of average photoelectric current as is obtained for the fully fatigued state of the cell in the case of continuous illumination of the same average value. This fatigue must not be confused with any slow changes in sensitivity which occur over comparatively long periods.

The non-linearity of photoelectric cells may be thus accounted for by this hypothesis of a fatigue and recovery during the periods of illumination and occultation. That this supposition is reasonable is shown by the following tests. The thermionic bridge was balanced for a given steady illumination. The galvanometer circuit was then broken, whilst the cell was covered for varying lengths of time. The cell was then exposed, and the galvanometer circuit completed after lengths of time varying from one half to five seconds. Quite distinctive galvanometer kicks were obtained after the short intervals of less than one second, and it was not until the interval reached five seconds that no deflexion was obtained. This is a point that requires further investigation.

The authors desire to express their indebtedness to Dr. J. W. J. Walsh and Professor A. O. Rankine for continued interest and advice during the work and to Mr. C. J. MacManus for extremely valuable assistance in taking observations.

XCVI. *Talbot's Law, Fatigue, and Non-Linearity in Photoelectric Cells.* *By* W. S. Stiles, *B.Sc.* (*National Physical Laboratory*) *.

Summary.

The problem considered is that of the average response of a photoelectric cell, when illuminated with flickered light. The response of the cell is assumed to be subject to short-period fatigue and recovery. The following points are discussed: (1) the variation of average response with sector speed, (2) the relation between the existence of short-period fatigue in a cell and the obedience of the cell to Talbot's law, (3) the form of the steady response—steady illumination characteristic for a cell obeying Talbot's law.

1. *Introduction.*

In the preceding paper Harrison and Carruthers† describe some experiments which aim at testing the applicability of Talbot's law to photoelectric cells. They find the law to hold good even in the case of certain non-linear cells, and to explain this rather unexpected result make the suggestion that the non-linearity of these cells is due to what may be termed short-period fatigue, *i. e.* fatigue which occurs in the first few seconds after switching on the light. The following analysis of the relations between Talbot's law, fatigue, and non-linearity was worked out by the writer after discussing with Harrison and Carruthers the results of their experiments. It is shown that, making the "natural" assumptions about the form of the fatigue and recovery curves, obedience to Talbot's law implies that the initial response of the cell is proportional to the light-intensity, and that in the case of non-linear cells the total amount of the fatigue is proportional to the square of the light-intensity.

2. *Average Current for a Given Light-intensity and Variable Sector Speed and Sector Angle.*

Consider a cell which has been rested for a long period in the dark. On exposing it to light-intensity I, the photo-

* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

† "Application of Talbot's Law to Photoelectric Cells with a Non-Linear Illumination-Current Characteristic."

electric current * obtained will not in general be a constant, but will vary with time owing to fatigue effects. The current at a time τ, after switching on the light, may be represented by a function $\phi(\tau)$. $\phi(\tau)$ defines the fatigue curve of the cell. In the case of most cells, after the light has been on for some time the photoelectric current will have settled down to a steady value. The slow change in the current which occurs for exposures of an hour or more is not taken into account in the present analysis, the fatigue under consideration here being over in the first few seconds of the exposure. When the steady state has been reached, if the light be cut off, the cell will gradually recover. The course of the recovery process can be represented by the function $\chi(\tau)$, which equals the current obtained if the light is switched on after τ seconds of recovery from the fully fatigued state. It will now be assumed (*a*) that if the cell is recovering and on switching on the light the current obtained is i, then the subsequent fatigue will be represented by $\phi(\alpha+\tau)$, where α is such that $\phi(\alpha)=i$; and (*b*) that if the light is on, and the current equals i, then on switching off the light the recovery will follow the law $\chi(\beta+\tau)$, where β is such that $i=\chi(\beta)$.

When the cell is periodically illuminated to the intensity I by means of a sector disk, a steady state is arrived at finally and a certain average current is obtained. Suppose the light is exposed for an interval L and cut off for an interval D, and suppose the currents at the initial and final instants of the light period are u and v respectively. Let α and β be such that $\phi(\alpha)=u$, $\chi(\beta)=v$. It follows that

$$v=\phi(\alpha+\mathrm{L}) \quad \text{and} \quad u=\chi(\beta+\mathrm{D}).$$

Thus

$$\left.\begin{aligned}\chi(\beta) &= \phi(\alpha+\mathrm{L}),\\ \phi(\alpha) &= \chi(\beta+\mathrm{D}).\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Given the fatigue and recovery curves, these equations suffice to determine α and β. The average current will be given by

$$\bar{i}=\frac{1}{\mathrm{L}+\mathrm{D}}\int_0^{\mathrm{L}}\phi(\alpha+t)\,dt.$$

* In the case of a cell in which the dark current is not zero, by the photoelectric current will be meant the excess over the dark current. It will then be assumed that the dark current is independent of the state of fatigue of the cell. It is probable that the dark current in most cells is due to electrical leakage over the glass, in which case the assumption just made is certainly true.

The periods L and D can be expressed in terms of the constants ω, r, and frequency n of the sector disk. Suppose this to have r openings of angle ω radians, then

$$L = \frac{1}{n}\frac{\omega}{2\pi}, \qquad D = \frac{1}{n}\frac{2\pi - r\omega}{2\pi r}.$$

By adding the two equations for α and β given above, it follows that

$$\phi(\alpha) - \phi(\alpha + L) = \chi(\beta + D) - \chi(\beta)$$

or

$$\frac{\phi(\alpha + L) - \phi(\alpha)}{L} = -\frac{D}{L}\left\{\frac{\chi(\beta + D) - \chi(\beta)}{D}\right\}.$$

Thus the portions of the fatigue and recovery curves along which the cell moves are such that the average slope of the fatigue curve over the light period equals the average slope of the recovery curve over the dark period times minus the ratio of the dark to the light period. When the sector speed is sufficiently high, L and D become very small and the average slopes can be replaced by differential coefficients. In this case

$$\phi'(\alpha) = -\frac{D}{L}\chi'(\beta) \quad \text{and} \quad \bar{i} = \frac{L}{L + D}\phi(\alpha) = \frac{\omega r}{2\pi}\phi(\alpha).$$

When the sector is not rotated at a very high speed, the average current will depend on the speed. Suppose for a given sector the values of α and β for infinite sector speed are α_0 and β_0, so that

$$\phi(\alpha_0) = \chi(\beta_0) \quad \text{and} \quad \phi'(\alpha_0) = -\frac{D}{L}\chi'(\beta_0).$$

For a finite sector speed put

$$\alpha = \alpha_0 + a, \qquad \beta = \beta_0 + b,$$

where a and b depend on n. Expanding the expression $\phi(\alpha + L)$ up to the second differential coefficient, we have approximately

$$\begin{aligned}\phi(\alpha + L) &= \phi(\alpha_0 + a + L) \\ &= \phi(\alpha_0) + (a + L)\phi'(\alpha_0) + \tfrac{1}{2}(a + L)^2\phi''(\alpha_0),\end{aligned}$$

and similar expressions for $\phi(\alpha)$, $\chi(\beta)$, and $\chi(\beta + D)$. Substituting in the equations (1) above, two simultaneous equations for a and b are obtained:

$$(a + L)\phi'(\alpha_0) + \tfrac{1}{2}(a + L)^2\phi''(\alpha_0) = b\chi'(\beta_0) + \frac{b^2}{2}\chi''(\beta_0),$$

$$a\phi'(\alpha_0) + \tfrac{1}{2}a^2\phi''(\alpha_0) = (b + D)\chi'(\beta_0) + \frac{(b + D)^2}{2}\chi''(\beta_0).$$

The approximate solution of these equations gives

$$a = -\frac{L}{2}\left\{1 - \frac{D}{4}\frac{\chi''(\beta_0)}{\phi'(\alpha_0)}\left(\frac{D}{L}\right)\right\}.$$

Now

$$\bar{i} = \frac{1}{L+D}\int_0^L \phi(\alpha+t)\,dt$$

$$= \frac{1}{L+D}\int_0^L dt\left\{\phi(\alpha_0) + (a+t)\phi'(\alpha_0) + \frac{(a+t)^2}{2}\phi''(\alpha_0)\right\}$$

On performing the integration and substituting the value of a found above, the average current is obtained in the form:

$$\bar{i} = \bar{i}_0\left[1 + \frac{1}{8n^2}\frac{\omega^2}{4\pi^2}\left\{\frac{1}{3} + \frac{\chi''(\beta_0)}{\phi''(\alpha_0)}\frac{D^2}{L^2}\right\}\frac{\phi''(\alpha_0)}{\phi(\alpha_0)}\right], \quad (2)$$

where $\bar{i}_0$ is the average current for infinite sector speed. It will be noticed that the effect of slowing down the sector is proportional to the square of the reciprocal of the sector frequency, and may be expected to be small. Experimentally, for sector speeds sufficiently low to detect the effect, the integrative action of the measuring system is no longer perfect, and the accuracy of the measurements falls off accordingly. It might be possible, however, to modify the apparatus to meet this difficulty; in which case the above equation would be of use in determining the shape of the fatigue and recovery curves. When certain natural assumptions are made about the fatigue effect, the result takes on a considerably more "workable" form. (See below, paragraph 4.)

3. *Talbot's Law.*

The above considerations have applied to the case of a cell exposed to a fixed illumination I flickered with a sector disk of given characteristics. For different illuminations I, the functions ϕ and χ will be different, and this may be indicated explicitly by writing $\phi(\tau, I)$ and $\chi(\tau, I)$. In what follows we are concerned solely with the average current at infinite sector speed, *i. e.*, $\frac{\omega r}{2\pi}\phi(\alpha, I)$, where α is defined by

$$\phi(\alpha, I) = \chi(\beta, I) \quad \text{and} \quad \phi_\tau'(\alpha, I) = -\frac{D}{L}\chi'(\beta, I).$$

The experiments of Harrison and Carruthers establish the validity of Talbot's law for both linear and non-linear cells.

The law takes in the present notation the following simple form:

$$\frac{\omega r}{2\pi}\phi(\alpha, \mathrm{I}) = \phi\left(\infty, \frac{\omega r}{2\pi}\mathrm{I}\right) \quad . \quad . \quad . \quad . \quad (3)$$

for any value of $\frac{\omega r}{2\pi} \leq 1$ and for all values of I.

For a linear cell,

$$\phi(\infty, \mathrm{I}) = k\mathrm{I};$$

thus

$$\frac{\omega r}{2\pi}\phi(\alpha, \mathrm{I}) = k\frac{\omega r}{2\pi}\mathrm{I}$$

or

$$\phi(\alpha, \mathrm{I}) = k\mathrm{I}.$$

It follows that

$$\phi_\tau'(\alpha, \mathrm{I})\frac{d\alpha}{d\omega r} = 0$$

and $\phi_\tau'(\alpha, \mathrm{I})$ must be zero, for otherwise $\frac{d\alpha}{d\omega r} = 0$ is inconsistent with the equations determining α. Thus the truth of the law implies in the case of a linear cell the absence of fatigue (short period). It also follows necessarily that if the cell is non-linear, fatigue must occur, for then

$$\phi(\alpha, \mathrm{I}) = \frac{\phi\left(\infty, \frac{\omega r}{2\pi}\mathrm{I}\right)}{\omega r/2\pi}$$

will vary with ωr, which can only take place through a variation of $\phi(\alpha, \mathrm{I})$ with α.

Talbot's law has enabled, therefore, a qualitative connexion to be established between fatigue and non-linearity. By making two plausible assumptions about the functions ϕ and χ, the quantitative relationship between the two effects is obtained in a very simple form.

Assumption A.

$$\phi(\tau, \mathrm{I}) + \chi(\tau, \mathrm{I}) = \phi(0, \mathrm{I}) + \phi(\infty, \mathrm{I}). \quad . \quad . \quad (4)$$

This makes the recovery process vary with the time in the same way as the fatigue process, except that it is in the opposite direction, *i. e.*,

$$\phi_\tau'(\tau, \mathrm{I}) = -\chi_\tau'(\tau, \mathrm{I}), \qquad \phi_\tau''(\tau, \mathrm{I}) = -\chi_\tau''(\tau, \mathrm{I}), \text{ etc.}$$

The equations determining α are now

$$\phi(\alpha, \mathrm{I}) = \{\phi(0, \mathrm{I}) + \phi(\infty, \mathrm{I})\} - \phi(\beta, \mathrm{I})$$

and

$$\phi_\tau'(\alpha, \mathrm{I}) = \frac{\mathrm{D}}{\mathrm{L}} \phi_\tau'(\beta, \mathrm{I}).$$

Assumption B.

$$\phi(\tau, \mathrm{I}) = \{\phi(0, \mathrm{I}) - \phi(\infty, \mathrm{I})\} e^{-\eta\tau} + \phi(\infty, \mathrm{I}). \quad . \quad (5)$$

This says that the fatigue follows an exponential law with the time; η may vary with I. It follows from the α equations that

$$\mathrm{D}/\mathrm{L} = e^{-\eta(\alpha-\beta)}$$

and

$$e^{-\eta\alpha} + e^{-\eta\beta} = 1,$$

from which is obtained

$$e^{-\eta\alpha} = \mathrm{D}/(\mathrm{D}+\mathrm{L})$$

and

$$\phi(\alpha, \mathrm{I}) = \phi(\infty, \mathrm{I}) + \{\mathrm{D}/(\mathrm{D}+\mathrm{L})\}\{\phi(0, \mathrm{I}) - \phi(\infty, \mathrm{I})\}.$$

Here

$$\phi(0, \mathrm{I}) - \phi(\infty, \mathrm{I}) = \mathrm{F}(\mathrm{I})$$

is the total fatigue. The experimental law (3) now takes the form:

$$\sigma\phi(\infty, \mathrm{I}) + \sigma(1-\sigma)\,\mathrm{F}(\mathrm{I}) = \phi(\infty, \sigma\mathrm{I}). \qquad \left[\frac{\omega r}{2\pi} = \sigma\right]$$

$\phi(\infty, \mathrm{I})$ is a function known experimentally, and hence

$$\mathrm{F}(\mathrm{I}) = \frac{\phi(\infty, \sigma\mathrm{I})}{\sigma(1-\sigma)} - \frac{\phi(\infty, \mathrm{I})}{1-\sigma} \quad . \quad . \quad . \quad . \quad (6)$$

is determinable. The left-hand side of this equation does not contain σ. A test of the validity of assumptions A and B is afforded by seeing whether $\phi(\infty, \mathrm{I})$ depends on I in such a way that $\dfrac{\phi(\infty, \sigma\mathrm{I})}{\sigma(1-\sigma)} - \dfrac{\phi(\infty, \mathrm{I})}{1-\sigma}$ is invariant with respect to σ. Suppose, further, $\mathrm{I}' = s\mathrm{I} (s \leq 1)$, then

$$\mathrm{F}(\mathrm{I}') = \frac{\phi(\infty, u\mathrm{I}')}{u(1-u)} - \frac{\phi(\infty, \mathrm{I}')}{1-u} = \frac{\phi(\infty, us\mathrm{I})}{u(1-u)} - \frac{\phi(\infty, s\mathrm{I})}{1-u},$$

and substituting for $\phi(\infty, us\mathrm{I})$ and $\phi(\infty, s\mathrm{I})$ the values obtained from (6) above with $\sigma = us$ and $\sigma = s$ respectively, we obtain

$$\mathrm{F}(\mathrm{I}') = \mathrm{F}(s\mathrm{I}) = s^2\mathrm{F}(\mathrm{I}).$$

The only function for which this is true for all values of s is $F(I)=RI^2$, where R is a constant. Thus

$$RI^2 = \frac{\phi(\infty, \sigma I)}{\sigma(1-\sigma)} - \frac{\phi(\infty, I)}{1-\sigma}.$$

By differentiating partially with respect to σ and I, $\phi(\infty, \sigma I)$ and σ can be eliminated and a differential equation obtained for $\phi(\infty, I)$, which runs:

$$I\frac{d\phi}{dI} - \phi + RI^2 = 0.$$

The general solution of this equation is

$$\phi(\infty, I) = kI - RI^2, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where k is a constant. This gives the final response of the cell after the first few seconds, as a function of the light-intensity. The initial response is obtained by substituting for $\{\phi(0, I) - \phi(\infty, I)\} = F(I)$ and $\phi(\infty, I)$ in equation (5), and putting τ equal to zero. We find that

$$\phi(0, I) = kI.$$

In the case of a so-called non-linear cell, therefore, obedience to Talbot's law implies that the initial response of the cell is linearly proportional to the light-intensity, but that short-period fatigue occurs which reduces the current by an amount proportional to the square of the light-intensity.

Harrison and Carruthers (*loc. cit.*) give measurements of the final response characteristics of a potassium neon-filled cell for which they also establish the applicability of Talbot's law. Their results are reproduced in columns 1 and 2 of Table I.

Table I.

I, arb. units.	$\phi(\infty, I)$, arb. units.	$kI - \phi(\infty, I)$.	$\frac{1}{I^3}\{kI - \phi(\infty, I)\} = R$.
1/12	·0933	(0)	—
1/8	·1377	·0023	·147
1/6	·1836	·0030	·108
1/4	·2709	·0090	·144
1/3	·3565	·0167	·150
1/2	·5232	·0366	·146
2/3	·6867	·0597	·134
3/4	·7643	·0754	·134
1	1·000	·1196	·120

According to equation (7),

$$\left.\frac{d\phi(\infty, \mathrm{I})}{d\mathrm{I}}\right|_{\mathrm{I}=0} = k,$$

and an approximate value for k is obtained, using the measured response at $\mathrm{I}=1/12$, and treating the characteristic as linear between $\mathrm{I}=0$ and $\mathrm{I}=1/12$. k then comes out to be 1·120. Columns 3 and 4 of the table give

$$k\mathrm{I}-\phi(\infty, \mathrm{I}) \quad \text{and} \quad \frac{1}{\mathrm{I}^2}\{k\mathrm{I}-\phi(\infty, \mathrm{I})\} = \mathrm{R}$$

for different values of I. The approximate constancy of the figures in the last column provides a general confirmation of the argument developed above.

4. *Further Remarks on the Average Current at Finite Sector Speeds.*

The formula (2) of paragraph 2 may be re-written

$$\bar{i} = \bar{i}_0\left[1+\frac{1}{8n^2}\frac{\sigma}{r^2}\frac{\phi''(\alpha_0)}{\bar{i}_0}\left\{\frac{1}{3}+\left(\frac{1-\sigma}{\sigma}\right)^2\frac{\chi''(\beta_0)}{\phi''(\alpha_0)}\right\}\right].$$

An experimental check of this result could be obtained by determining the variation with sector speed for two sectors having the same σ value but with different numbers of openings r. The functions $\phi''(\alpha_0)$ and $\chi''(\beta_0)$ depend only on σ, so that the coefficient of $\frac{1}{n^2}$ should vary as $\frac{1}{r^2}$.

Theoretically, if the coefficient of $\frac{1}{n^2}$ can be determined experimentally, the form of the fatigue and recovery curves can be deduced. For in that case

$$\frac{\phi''(\alpha_0)}{3}+\frac{(1-\sigma)^2}{\sigma^2}\chi''(\beta_0)$$

will be an experimentally determined function of σ, and the same is true of

$$\phi(\alpha_0) = \chi(\beta_0) = i_0/\sigma.$$

Calling these functions $g(\sigma)$ and $f(\sigma)$ respectively, and making use of the equation

$$\phi'(\alpha_0) = \frac{\sigma-1}{\sigma}\chi'(\beta_0),$$

the following differential equation is obtained for σ in terms of α_0:

$$\frac{4}{3}f'(\sigma)\frac{d^2\sigma}{d\alpha_0^2}+\left(\frac{d\sigma}{d\alpha_0}\right)^2\left\{\frac{4}{3}f''(\sigma)-\frac{1}{\sigma(\sigma-1)}f'(\sigma)\right\}=g(\sigma).$$

The solution of this equation appropriate to the boundary conditions $\sigma=0$ when $\alpha_0=0$, $\sigma=1$ when $\alpha_0=\infty$ may be written

$$\sigma = \mathrm{N}(\alpha_0),$$

and the fatigue curve is obtained immediately as

$$\phi(\alpha_0)=f(\sigma)=f\{\mathrm{N}(\alpha_0)\}.$$

The recovery curve is determinable by an analogous method.

If the two assumptions of paragraph 3 restricting the possible shape of the recovery and fatigue curves are adopted,

$$g(\sigma)=\frac{\phi''(\alpha_0)}{3}+\left(\frac{1-\sigma}{\sigma}\right)^2\chi''(\beta_0)=\eta^2\mathrm{F(I)}\frac{(1-\sigma)(4\sigma-3)}{3\sigma}$$

or

$$\eta^2\mathrm{F(I)}=\{3\sigma/(1-\sigma)(4\sigma-3)\}g(\sigma).$$

The left-hand side of the last equation does not contain σ, and the constancy of $\dfrac{3\sigma g(\sigma)}{(1-\sigma)(4\sigma-3)}$ determined experimentally for different values of σ would provide a further check on the assumptions A and B. No restriction has been placed on η, *i. e.*, the rapidity of the fatigue process may be different for different illuminations I. The present method enables any such variation to be detected, for $\mathrm{F(I)}=\mathrm{I^2R}$ and $\eta^2\mathrm{F(I)}$ as a function of I is given by measurements of $g(\sigma)$ at different illuminations.

5. *Conclusion.*

The above considerations apply specifically to the case of photoelectric cells. It is clear, however, that the *analysis* is also valid for selenium cells * and, in fact, for all cases in which the average response to a periodically interrupted stimulus is in question. There are, however, difficulties about applying the results to human vision.

* Further experimental work by Harrison and Carruthers indicates that in certain cases Talbot's law is also valid for selenium cells.

XCVII. *The Propagation of Sound in Gases* *.

By D. G. Bourgin, *Ph.D., University of Illinois, U.S.A.* †

DURING the last few years attention has again been drawn to the propagation of sound in gases—particularly at high frequencies. The experimental work of principal consequence as regards the purposes of this paper is that of Pierce ‡ and Abello §, and within the year there has appeared a valuable theoretical study by Herzfield and Rice ‖.

An early edition of Jeans' 'Dynamical Theory of Gases' contains a treatment of the propagation of sound in a pure gas, recognizing the lag in the exchange of translational and internal energy for the case of a system of loaded spheres. Herzfeld and Rice's article deals with the extension of this hypothesis to the general case, and it is assumed that there is a uniform lag for all internal energy transfers. The present paper, begun some months before the publication of their results, makes an attempt to link up explicitly the nature of the kinetics of sound with the internal constitution of the entities composing the gas.

The first part of this work develops the ideas and equations for a theory which takes account of the collision excitation and de-excitation of the molecules composing the gas. In brief, it is assumed that under the influence of collisions of the first kind some molecules are thrown into states of higher energy from which they may return to lower energy levels either spontaneously or as the outcome of collisions of the second kind.

To fix our ideas, let us consider a gas maintained at the constant temperature T_0. The propagation of a sound-wave implies the possibility of distinguishing regions of higher and regions of less kinetic energy than the mean in the gas. For purposes of exposition we will make use of the fiction of a correlated regional translational temperature. During the perturbation of the gas we may characterize each internal state i by another fictitious temperature T_i, defined as that temperature which under equilibrium conditions associates the same number of molecules in state i.

* D. G. Bourgin, 'Nature,' cxxii. p. 133 (1928).

† Communicated by the Author.

‡ G. W. Pierce, Am. Acad. Sci. lx. p. 271 (1925).

§ T. P. Abello, Proc. Nat. Acad. xiii. p. 699 (1927); Phys. Rev. Jun 1926, p. 1083.

‖ K. F. Herzfeld and F. O. Rice, Phys. Rev. xxxi. p. 691 (1928).

For low frequencies the collision mechanism is adequate to permit of exact reproduction in the internal temperatures of the pulsations in the translational temperature. At higher frequencies there is a phase-lag and then a diminution in the relative amplitudes of the several internal and the translational temperatures. These various phase-lags and the amplitude diminutions affect the absorption and decrease the effective specific heat — accordingly increasing the velocity of propagation of sound in the gas.

The Herzfeld-Rice hypothesis is also touched on as a special case of this theory, and some of the implications not hitherto exhibited are mentioned. The theory is in all respects a kinetic theory, and the agencies taken account of (exclusive of radiation) are all described in terms of their kinetic equivalents.

The second part of the paper advances a theory of sound propagation in a mixture of two gases. So far as the author is aware, this represents the first attempt to consider this problem. The theory is immediately applicable to experimental results of the type obtained by Pierce and Abello, and suggests the desirability of experimental researches to test the conclusions arrived at.

Part I.

We shall have occasion to make use of the following symbols :—

K = kinetic energy of translation of a single molecule.

$\delta\mathrm{T}$ = increment in translational temperature.

$\delta\mathrm{T}_i = \omega_i\,\delta\mathrm{T}$ = increment in internal temperature of state i.

m = mass of gas molecule.

N_i = numerical concentration of the molecules/c.c. in state i.

N = numerical gas density.

ϵ_i = energy of the level i.

$\epsilon_{ij} = \epsilon_i - \epsilon_j$.

$\nu = \nu/2\pi$ = sound frequency.

$\bar{\lambda} = 2\pi\lambda$ = sound wave-length in gas.

u = variable molecular velocity in the x direction.

v = mass velocity in the x direction.

$\mathrm{V} = \nu\lambda$ = velocity of sound propagation.

The essential equations may now be written :—

The equation of continuity is

$$\frac{d}{dt}\mathrm{N} = -\frac{\partial}{\partial x}\mathrm{N}v. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The equation for the momentum transfer,

$$\frac{d}{dt}m\mathrm{N}v = -\frac{\partial}{\partial x}m\mathrm{N}\overline{u^2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$= -\frac{2}{3m}\frac{\partial}{\partial x}\mathrm{KN}, \quad . \quad . \quad . \quad . \quad (2.1)$$

where the bar denotes a regional average.

The statement of the change in the concentration N_i,

$$\frac{d}{dt}\mathrm{N}_i = -\frac{\partial}{\partial x}\mathrm{N}_i v + \Delta\mathrm{N}_i, \quad . \quad . \quad . \quad . \quad (3)$$

where $\Delta\mathrm{N}_i$ refers to the effect of collisions. A check on equation (3) is afforded by summing over the subscript i, for, since $\Sigma\Delta\mathrm{N}_i = 0$, we obtain equation (1).

Finally, the variation in kinetic energy is expressed *,

$$\frac{d}{dt}\mathrm{NK} = -\frac{\partial}{\partial x}\frac{5}{3}v\mathrm{K} + \Delta\mathrm{K}, \quad . \quad . \quad . \quad . \quad (4)$$

where $\Delta\mathrm{K}$ represents the net contribution of the internal states or, otherwise stated, is the difference between the energy transfers arising from collisions of the first and second kinds respectively.

An expression for $\Delta\mathrm{N}_i$ more amenable to analysis is derived as follows :—

The principle of microscopic reversibility asserts that at equilibrium

$$\mathrm{N}_i^2[\bar{f}_{ij} - f_{ij}] + \mathrm{N}\mathrm{N}_i f_{ij} - \mathrm{N}_j^2[\bar{f}_{ji} - f_{ji}] + \mathrm{N}\mathrm{N}_j f_{ji} = 0, \quad (5)$$

where $\bar{f}_{ij}$ is the averaged probability of the transition $i \rightarrow j$ when the colliding molecules are similarly specified, and f_{ij} refers to the case that they are in different states, thus taking account of the possible coupling or resonance effect †

* The $\frac{5}{3}$ arises from averaging $u\mathrm{K}$. *Cf.* Jeans's 'Kinetic Theory of Gases.'

† For many gases there is no appreciable coupling and the coefficients of the squared terms vanish (though there is no corresponding simplification in any of the later formulæ based on equation (5)). *Cf.*, for instance, HCl.

between molecules in similar states. The symbols $\bar{f}_{ji}$ and f_{ij} are the probabilities for the reverse * encounters.

Attendant on the passage of a sound-wave the translational energy perturbations affect the probability factors f_{ij} etc., while the fluctuations in N_i are determined by the variations in the internal temperatures, i. e., $\omega_i \delta T$. Hence we may write the collision contribution to the change † in N^i as

$$\Delta N_i = -\sum_j \delta N[N_i f_{ij} - N_j f_{ji}] + \delta N_i[2\bar{f}_{ij} - f_{ij}]N_i + N f_{ij} - \delta N_j[(N_j(2)(\bar{f}_{ji} - f_{ji}) + N f_{ji}] + N_i^2 \delta[\bar{f}_{ij} - f_{ij}] + N N_i' \delta f_{ij} - \ldots \quad (5.1)$$

Evidently

$$\delta N_i = \frac{\delta N}{N} N_i + \dot{N}_i \omega_i \delta K, \quad (6)$$

the symbol $\dot{N}_i$ being interpreted as $\frac{dN_i}{dK}$.

The variations in the probability factors are of the form $\frac{\partial f_{ij}}{\partial K}\delta K$. On introducing the abbreviation

$$R_{ij} = N\left[2\frac{N_i}{N}(\bar{f}_{ij} - f_{ij}) + f_{ij}\right],$$

and observing that for $\omega_i' = 1$, $\Delta N_i = 0$, we write

$$\sum_j N[\delta N_i R_{ij} - \delta N_j R_{ji}] = -\Sigma(N N_i - N_i^2)\delta f_{ij} - [N_j N - N_j^2]\delta f_{ji} + N_i^2 \delta f_{ij} - N_j^2 \delta f_{ji}. \quad (5.2)$$

Substituting equation (6) in equation (5.1), and noting that the coefficient of δN becomes precisely the left side of equation (5) and is therefore 0, we have, finally,

$$\Delta N_i = -N \sum_j [\dot{N}_i R_{ij}(\omega_i - 1) - \dot{N}_j R_{ji}(\omega_j - 1)]\delta K.$$

* P.A.M. Dirac, Proc. Soc. of London, cvi. A, p. 581 (1914).

† The matter of determining the proper sign, both here and later in equation (7), requires some care. In order to establish the negative sign above, it is observed that $N_i[\ ] - N_j[\ ]$ ($N_i[\ ]$ and $N_j[\ ]$ are no longer to be considered equilibrium values) is the difference between the number of molecules leaving the state i for the state j, and *vice versâ*. Accordingly $N_i[\ ] - N_j[\ ] > 0$ implies a diminution in N_i. Since positive ΔN_i represents an increase, the negative sign is a consequence.

The collision increment in K is equal to, and opposite in sign to, the increment in internal energy. Therefore

$$\Delta K = -\sum_i \Delta N_i \epsilon_i$$

$$= N \sum_{i\,j} \Sigma (\dot{N}_i R_{ij}(\omega_i - 1) - \dot{N}_j R_{ji}(\omega_j - 1))\epsilon_i. \quad . \quad (7)$$

Restricting attention to sound-waves of small amplitude, we may approximate the solution for equations (1)–(4) by assuming that all the dependent variables entering our equations vary harmonically about their mean values, *i. e.*,

$$X = X_0 + \Im \mid \delta X \mid e^{-j(\nu t - x/\lambda)}, \quad j = \sqrt{-1}, \quad . \quad (8)$$

where $\Im$ refers to the imaginary part of the succeeding expression. We next remark that because of the smallness of v we may neglect products of the type $v \mid \delta X \mid$; hence the operator $\frac{d}{dt}$ may be replaced in our work by $\frac{\partial}{\partial t}$.

Our first interest is the determination of N_i. The system (3) becomes

$$j\nu \left[\frac{\mid \delta N \mid}{N} N_i + \dot{N}_i \omega_i \mid \delta K \mid \right] = j \frac{\mid \delta v \mid}{\lambda} N_i + \Delta N_i e^{-j(\nu t - x/\lambda)}. \quad (3.1)$$

Since equation (1) may be written

$$j\nu \delta N = j \frac{\mid \delta v \mid}{\lambda} N, \quad . \quad . \quad . \quad . \quad . \quad (1.1)$$

we have for equation (3.1)

$$j\nu \dot{N}_r \omega_r \mid \delta K \mid = -\sum_s [\dot{N}_r R_{rs}(\omega_r - 1) - \dot{N}_s R_{sr}(\omega_s - 1)] \mid \delta K \mid.$$

$$. \quad . \quad . \quad (3.2)$$

Let

$$\omega_s = a_{s0} + a_{s1}\nu + a_{s2}\nu^2 + \ldots . \quad . \quad . \quad . \quad (9)$$

Kinetic theory assures us that for vanishing frequencies the internal and translational temperatures are equal, i. e., $a_{s0} = 1$. The same conclusion may be arrived at, incidentally, on substituting equation (9) in equation (3.2) and equating to zero the coefficients of like powers of ν. For the constant term there results

$$\sum_s (a_{r0} - 1)\dot{N}_r R_{rs} - (a_{s0} - 1)\dot{N}_s R_{sr} = 0.$$

This is true for $r = 1, \ldots, n$; it follows* that $a_{r0} \equiv \underset{r}{1}$.

For the coefficient of ν we get

$$j\dot{N}_r a_{r0} + N\sum_s \dot{N}_r R_{rs} a_{r1} - \dot{N}_s R_{sr} a_{s1} = 0, \qquad r = 1, \ldots, n. \quad (9.1)$$

Hence

$$a_{s1} = (-1)^n j \sum_{r=1}^{n} \dot{N}_r \bar{H}_{rs}/N\Delta, \quad . \quad . \quad . \quad . \quad (10)$$

where $\bar{H}_{rs}$ is the cofactor of a_r, the term in the sth column and rth row in the determinant Δ. We will show now that this is

$$a_{s1} = -j \left| \sum_{r=1}^{n} \dot{N}_r \bar{H}_{rs}/N\Delta \right| . \quad . \quad . \quad (10.1)$$

First, we observe that all the elements of the two determinants are real. On referring back to equation (8.1), it is clear that in any given column there are one positive and $n-1$ negative elements—since the numerator determinant differs from Δ in that the sth column has been replaced by n negative terms, our result is established.

We have shown, then, that a_{s1} is negative and imaginary, so that the first effect of increasing frequency is the introduction of a *lag* into the relation between translational and internal fluctuations.

The equations obtained by equating the coefficients of higher powers of ν to 0 differ from equation (9.1) only in that a_{s1} is replaced by a_{sq}, and a_{s0} by $a_{s,q-1}$. The formal solution of these recurrence relations is

$$a_{sq} = (-j)^q \left| \frac{\sum_{\alpha_1} \cdots \sum_{\alpha_q} \dot{N}_{\alpha_1} \cdots \dot{N}_{\alpha_q} \bar{H}_{\alpha_1 s} \bar{H}_{\alpha_2 \alpha_1} \cdots \bar{H}_{\alpha_n \alpha_{n-1}}}{N^q \Delta^q} \right|, \quad (10.2)$$

where the $\bar{H}$'s retain their earlier definition. It is seen that

* We have, in fact,

$$a_{r0} = \left| \begin{array}{lll} N_1 \sum_s R_{1s} & -N_2 R_{21} & -N_3 R_{31} \ldots \sum_s N_1 R_{1s} - N_s R_{s1} \ldots \\ -N_1 R_{12} & & \sum_s N_2 R_{2s} - N_s R_{s2} \ldots \\ -N_1 R_{13} & & \vdots \\ \ldots\ldots & & \end{array} \right| \Big/ \Delta.$$

On subtracting the sum of all the other columns from the rth column in the numerator determinant, we have precisely the denominator determinant.

the a's are alternately real and pure imaginary; hence, for instance, the amplitude diminution is a second-order effect.

ω_i may be developed in descending powers of ν; but, since at the very high frequencies at which such a development would be desirable irregularities are to be expected in the behaviour of the gas, it is not thought worth while to stress this aspect of the problem. We may remark in passing, however, that a computation, the details of which are delegated to an appendix, yields the expansion

$$\omega_m = -\frac{j}{\nu}\frac{A_m \mathrm{N}}{\dot{\mathrm{N}}_m} + \frac{\mathrm{N}^2}{\nu^2}\sum_s\left(\frac{A_s \mathrm{R}_{sm}}{\dot{\mathrm{N}}_m} - \frac{A_m \mathrm{R}_{ms}}{\dot{\mathrm{N}}_m}\right), \quad . \quad (11)$$

where

$$A_m = \sum_s \dot{\mathrm{N}}_m \mathrm{R}_{ms} - \dot{\mathrm{N}}_s \mathrm{R}_{sm}.$$

It may be easily verified that the expression for $\Delta\mathrm{K}$ can be written

$$\Delta\mathrm{K} = \mathrm{N}\sum_r\sum_s(\dot{\mathrm{N}}_r \mathrm{R}_{rs} a_{rq}\epsilon_{rs})\nu^q.$$

On taking account of equation (7.1), we may write equation (4) in the form

$$j\nu\{|\,\delta\mathrm{N}\,|\,\mathrm{K} + \mathrm{N}\,|\,\delta\mathrm{K}\,|\} = \left(\frac{5}{3}\right)\frac{\mathrm{NK}\,|\,\delta v\,|}{\lambda} + \sum_r\sum_s \mathrm{N}\nu^q a_{rq}\dot{\mathrm{N}}_r \mathrm{R}_{rs}\epsilon_{rs}. \quad . \quad . \quad . \quad (4.1)$$

Equation (2.1) may be expressed

$$\mathrm{N}\nu\,|\,\delta v\,| = \frac{2}{3\lambda m}(\mathrm{N}\,|\,\delta\mathrm{K}\,| + |\,\delta\mathrm{N}\,|\,\mathrm{K}). \quad . \quad . \quad (2.2)$$

On eliminating the moduli of the harmonic terms, there results

$$j\left[\frac{3m\mathrm{V}^2 - \frac{10}{3}\mathrm{K}}{3m\mathrm{V}^2 - 2\mathrm{K}}\right] = \sum_s\sum_r a_{sr}\nu^{r-1}\mathrm{B}_s, \quad . \quad . \quad (12)$$

where

$$\mathrm{B}_s = \sum_r \dot{\mathrm{N}}_r \mathrm{R}_{sr}\epsilon_{sr};$$

Recalling (equation (10.2)) that $a_{sr} = \frac{(-j)^r}{\mathrm{N}^r}\, b_{sr}$, b_{sr} real, we derive

$$\frac{1}{\mathrm{V}^2} = \frac{3m}{\mathrm{K}}\left[\frac{\mathrm{N} + (\sum_s\sum_r b_{sr}\nu^{r-1}\mathrm{B}_s/\mathrm{N}^{r-1})}{\frac{10}{3}\mathrm{N} + 2\sum_s\sum_r b_{sr}\nu^{r-1}\mathrm{B}_s/\mathrm{N}^{r-1}}\right]. \quad . \quad (12.1)$$

For low frequencies this reduces to

$$\frac{1}{\mathrm{V}_0^2} = \frac{3m}{\mathrm{K}}\left[\frac{\mathrm{N} + b_1\mathrm{B}}{\frac{10}{3}\mathrm{N} + 2b_1\mathrm{B}}\right], \quad . \quad . \quad . \quad . \quad (13)$$

where $$b_r = \sum_s b_{sr}B_s/\sum_s B_s = \sum_s b_{sr}B_s/B,$$

$3k\mathrm{B}\,\delta\mathrm{T}/2\mathrm{N}$ = change of energy / unit time / collision for a uniform temperature difference of $\delta\mathrm{T}$ between the translational and internal temperatures.

The Laplace formula for sound velocity may be written

$$\frac{1}{\mathrm{V}_0^2} = \frac{3m}{\mathrm{K}}\left[\frac{3+2\beta}{10+4\beta}\right], \quad . \quad . \quad . \quad . \quad (14)$$

where β stands for the number of internal degrees of freedom.

If we equate the values for V_0^2 given by equations (13) and (14), there results, after a little algebra,

$$b_1 = 2\beta\mathrm{N}/3\mathrm{B}$$
$$= \beta\mathrm{N}k/\mathrm{B}(d\mathrm{T}/d\mathrm{K}). \quad . \quad . \quad . \quad . \quad (15)$$

This relation * defines the mean time-lag in terms of the other constants of the gas, and is expected to hold exactly if β is determined from low-frequency data. At high frequencies the measured specific heat is different, and we may, in fact, write

$$\beta = \sum_{r=0}^{\infty} \beta_r \nu^r.$$

Equation (15) involves β_0.

The mean phase-lag in seconds is then $4\pi\beta/3\mathrm{B}$ seconds, or about $4\pi\beta\bar{\nu}/3\mathrm{B}$ cycles. Assuming the plausible † value $\mathrm{B} \sim 10^{-8}$, it seems that the average lag of internal fluctuation behind changes in translational motion is about 10^{-7} second.

The absorption depends on the imaginary terms in the expansion of $\dfrac{1}{\mathrm{V}}$ —to a first approximation :

$$\frac{1}{\mathrm{V}^2} = \frac{1}{\mathrm{V}_0^2}\left[1 - \frac{6j\nu\sum_s b_{s2}\mathrm{B}_{s2}}{\mathrm{N}^2(5+2\beta)(3+2\beta)}\right]; \quad . \quad . \quad (16)$$

$$\therefore \quad \frac{1}{\mathrm{V}} = \frac{1}{\mathrm{V}_0}\left[1 - \frac{3j\nu b_2 \mathrm{B}}{\mathrm{N}^2(5+2\beta)(3+2\beta)}\right]. \quad . \quad (16.1)$$

* A somewhat more direct method of deriving equation (15), though not the most obvious, for a first attempt is based on the fact that

$$\frac{d}{dt}\Sigma \mathrm{N}_r\epsilon_r = j\nu b_1 \mathrm{B}\exp j(\nu t - x/\lambda)$$
$$= j\nu\beta\mathrm{N}\frac{d\,\delta\mathrm{K}}{dt}.$$

† Based on the data given in Herzfeld & Rice's paper.

Similarly, taking account of the real terms, it is possible to find the amplitude diminution in response of internal temperature; we shall not, however, concern ourselves here with this continuation except to observe that this term would, of course, involve b_3 (and b_2).

Entirely analogously to the expansions at low frequencies we may develop asymptotic formulæ useful at super frequencies. We have, in fact,

$$\frac{1}{V^2} = \frac{9m}{10K}[1+2j\mathrm{B}/5\nu \ldots]$$

$$= \frac{1}{V_\infty^2}[1+2j\mathrm{B}/5\nu \ldots]. \quad . \quad . \quad . \quad (17)$$

V_∞ is the velocity for a gas with no internal degrees of freedom, and B has already been defined *.

Heretofore we have considered, in the interest of simplicity, merely the influence of collisions of the first and second kinds on the propagation of sound. Another agency in modifying our velocity and absorption is that of radiation. We may take account of this by redefining our R_{rs} and R_{sr} to be

$$N\bar{R}_{rs} = NR_{rs} + \rho(\bar{\nu}_{rs})B_{rs} \qquad \epsilon_s > \epsilon_r$$

$$= NR_{rs} + A_{rs} \qquad \epsilon_s < \epsilon_r, \quad . \quad (18)\dagger$$

where $\rho(\bar{\nu}_{rs})$ is the density of black-body radiation of frequency $\bar{\nu}_{rs}$ at the temperature T_0; B_{rs}, and A_{rs} are the well-known Einstein coefficients.

At ordinary temperatures the state $s(\neq 0)$ is usually one above the mean energy level; it is therefore an unstable state, and it seems likely that most collisions will result in transitions to lower energy levels. Certainly the permitted transitions for radiation changes are at least as likely as other collision transitions and, since the number of states

* A more complete expansion is derivable from equation (11); for terms only as far as $\frac{1}{\nu^2}$ we should use

$$\frac{1}{V^2} = \frac{3m}{K}\left[\frac{1+\frac{jB}{\nu} - \Sigma_s \frac{NA_sB_s}{\dot{N}_s\nu^2}}{\frac{\nu}{3}+2\left[j\frac{B}{\nu} - \Sigma_s \frac{NA_sB_s}{\dot{N}_s\nu^2}\right]}\right].$$

† At very high temperatures we must, of course, write for the case $\epsilon_r > \epsilon_s$,

$$N\bar{R}_{rs} = NR_{rs} + A_{rs}\left(1+\rho(\bar{\nu}_{rs})\frac{8\pi h\bar{\nu}_{rs}^3}{C^3}\right).$$

which contribute appreciably to the specific heat at ordinary temperatures is not very large, NR_{sr} is of the order of magnitude of the collision frequency to within a probable factor of 10^{-2} or so. At N.T.P, therefore, NR_{sr} would be 10^8 or greater.

Since for low temperatures

$$N_r B_{rs}\rho(\bar{\nu}_{rs}) \sim A_{sr}N_s,$$
$$N_r R_{rs} \sim R_{sr}N_s,$$

it follows that the relative importance of the types of changes out of state r, e. g. $(B_{rs}\rho(\bar{\nu}_{rs}) : NR_{rs})$ is the same as that of changes to the state r, e. g. $(A_{sr} : NR_{sr})$. The values of A_{sr}, for the states contributing appreciably to the specific heat, for many molecules (for instance, HCl) is of the order of 10^{-2}, so that the radiation terms may usually be neglected. At high temperatures or low densities the radiation effect becomes of increasing relative importance.

As regards viscosity, it is to be noticed that the term involving it would enter only in equation (4), and, to the approximation we are making, it would appear additively in the expression for the absorption coefficient. Its value, as given by Lord Rayleigh *, is $2\tau\nu^2/3mNV^3$, where τ is the coefficient of viscosity. Since the exponent for diminution of intensity is twice that for amplitude change, there results for the total fractional intensity change in a sound-wave after travelling the distance x,

$$\exp -\frac{8\pi^2\nu^2 x}{V}\left[3\{b_2 B/N^2(5+2\beta)(3+2\beta)\}+\{\tau/3mNV^2\}\right]. \quad . \quad . \quad . \quad (19)$$

Further detailed progress in the general theory depends on a knowledge of the R_{rs} probabilities †. Let us consider

* Rayleigh, 'Theory of Sound,' ii. par. 346.

† To indicate the nature of the difficulties in determining R_{rs} more clearly, we consider the correspondence principle aspect of the problem. If the electric moment of the molecule be expanded in inverse powers of ν, we may consider the various terms as being the contributions of a dipole, a superposed quadrupole, etc. For the case of radiation transition probabilities (the Einstein co-efficients) for, say, polar molecules only the 1st term's contribution is relatively important. In the case of the collision transition probabilities, the higher moments are almost of the same interest as the dipole contribution. Of course it is possible to work out our theory for an idealized case in which the higher moments are all 0—here the collision transition probabilities would be simply connected with the Einstein coefficients, but the results to be expected will hardly be of general application. *Cf.* in this connexion Nordheim, *Zeit. f. Physik*, xxxvi. p. 496 (1926).

now the Herzfeld-Rice assumption of a single internal temperature. This amounts in our work to writing

$$\omega_r \underset{r}{\equiv} \omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

It will be seen that this implies that equation (10.2) may be written

$$a_{sq} \underset{s}{\equiv} a_q = [-j\sum_{\alpha_1} \dot{N}_{\alpha_1} \bar{H}_{\alpha_1 s}/N\Delta]^q$$
$$= a^q. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20.1)$$

Hence, assuming the validity of equation (15), it would follow that

$$\omega = 1 - \frac{2}{3} j\nu \frac{\beta}{B} - \frac{4}{9} \frac{\beta^2}{B^2} \nu^2 + \ldots \quad . \quad . \quad . \quad (21)$$

The asymptotic expansion is here †

$$\omega = -jb_1 + \frac{b_1^2}{\nu^2}. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

It will be observed that the parameters in the expansions at super frequencies (*i. e.*, equation (11), note *, p. 829, equation (22)) are those involved in the expressions we have obtained for long wave-lengths.

It is important to remark that the extreme assumption $\omega_r \underset{r}{\equiv} \omega$ is unnecessary if the velocity for small frequencies be the question of interest, for in either case we have just one unknown parameter; but it does relate b_r $(r > 1)$ to b_1, and hence leads to more definite formulæ when higher-order effects, such as absorption or amplitude diminution of internal fluctuations, are investigated. It is clear, of course, that equation (20) can be only a rough sort of approxima-

† The same expansions are also easily derived from the fact that for ω_r independent of r

$$\omega_r \equiv \frac{NA_r}{j\nu\dot{N}_r + NA_r}$$
$$= 1 - j\nu \frac{\dot{N}_r}{NA_r} - \nu^2 \left(\frac{\dot{N}_r}{NA_r}\right)^2 + \ldots,$$

and also

$$= -\frac{j}{\nu} \frac{NA_r}{\dot{N}_r} + \frac{1}{\nu^2} \left(\frac{NA_r}{\dot{N}_r}\right)^2;$$

the coefficient of the term in $-j\nu$ is our previously-defined b_1, i. e.

$$b_1 = \frac{N_r}{A_r}, \quad \text{etc.}$$

tion to the truth, whose accuracy probably diminishes with increasing q, so that the predictions are those of order of magnitude only.

The diminution in amplitude of internal variations as compared with the changes in translational energy is of the order of

$$1-2\left(\frac{b_1}{\mathrm{N}}\right)\nu^2+\left(\frac{b_2}{\mathrm{N}}\right)^2 : 1$$

or

$$1-\frac{4\pi^2}{9}\left(\frac{\beta\nu}{\mathrm{B}}\right)^2 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Even for frequencies of 10^5 the diminution is expected to be negligible—accordingly the principal effect is the phase-lag. We may write equation (19) now as

$$\exp-\frac{8\pi^2\nu^2 x}{\mathrm{V}}\left[\frac{4}{3}\frac{\beta^2}{\mathrm{B}(5+2\beta)(3+2\beta)}+\frac{\tau}{3m\mathrm{N}\mathrm{V}^2}\right] . \quad (19{\cdot}1)$$

Part II.

The general problem of the propagation of sound-waves in mixed gases does not seem to have been treated previously. It is possible to extend our general theory involving different values of ω_r in a formal way—just as in the case of the pure gas it is feasible to obtain an expression for the velocity of propagation at low frequencies in terms of the mean phase displacement determined by relations analogous to equation (15) without further *ad hoc* assumptions; however, in order to exhibit the absorption we shall be forced to make simplifying hypotheses. For this reason we shall carry through the whole development on the basis of our restrictive hypotheses, bearing in mind the more general validity of our velocity formula.

Assume that in a mixture of gases A and B, the internal temperature variations of the two types of molecules are independent of the state considered, and may be characterized by the symbols $\omega_{\mathrm{A}}\delta\mathrm{T}$ for the molecules A, and $\omega_{\mathrm{B}}\delta\mathrm{T}$ for the B molecules. We shall use m_{A} and m_{B} to denote the respective masses, and N_{A} and $\mathrm{N}-\mathrm{N}_{\mathrm{A}}=\mathrm{N}_{\mathrm{B}}$ for the concentrations.

Applying the equation of continuity to each of the components, we have

$$\nu\,|\,\delta\mathrm{N}_{\mathrm{A}}\,| = \mathrm{N}_{\mathrm{A}}\,|\,\delta v\,|/\lambda,$$
$$\nu\,|\,\delta(\mathrm{N}-\mathrm{N}_{\mathrm{A}})\,| = (\mathrm{N}-\mathrm{N}_{\mathrm{A}})\,|\,\delta v\,|/\lambda. \quad . \quad . \quad (24)$$

To find the analogue of equation (1) we observe, first, that

the mass motion must be the same for the molecules of each gas, and, secondly, that the $\overline{u^2}$ occurring in equation (2) is to be replaced by $[N_A\overline{u_A^2}+(N-N_A)\overline{u_B^2}]/N$. Accordingly,

$$\frac{d}{dt}Nv=-\frac{\partial}{\partial x}\left[\frac{2}{3m_A}N_AK_A+\frac{2}{3m_B}(N-N_A)K_B\right]. \quad (25)$$

There is no collision term here because the condition for its appearance is a difference in mass motion.

The equipartition theorem asserts that

$$K_A=K_B=K.$$

Therefore

$$N\nu\,|\,\delta v\,|-\left[\frac{2}{3\lambda}\left\{\frac{1}{m_A}(|\,\delta N_A\,|\,K+N_A\,|\,\delta K\,|)+\frac{1}{m_B}(|\,\delta(N-N_A)\,|\,K+(N-N_A)\,|\,\delta K\,|)\right\}\right]. \quad (25.1)$$

On solving equation (25.1) simultaneously with equation (24)

$$\left.\begin{aligned}|\,\delta v\,|&=\frac{2VS\,|\,\delta K\,|}{3NV^2-2SK},\\ |\,\delta N\,|&=\frac{2N\lambda^2S\,|\,\delta K\,|}{3NV^2-2SK},\end{aligned}\right\} \quad (26)$$

where $$S=\frac{N_A}{m_A}+\frac{N-N_A}{m_B}=N\overline{m^{-1}}.$$

We shall use the symbols R_{rs}, P_{rs} for the transition probabilities associated with collisions of two A or two B molecules, and the same symbols capped with a bar to denote the correlated quantities in an AB-type collision. With this understanding,

$$\Delta K=|\,\delta K\,|\,[(\omega_A-1)\{N_A\Sigma_r\Sigma_s N_A\dot{N}_{Ar}R_{rs}\epsilon_{rs}+(N-N_A)\bar{R}_{rs}\epsilon_{rs}\dot{N}_{Ar}+(\omega_B-1)\{\Sigma_p\Sigma_q(N-N_A)(\overline{\dot{N}-\dot{N}_A})_pP_{pq}\epsilon_{pq}+N_A(\overline{\dot{N}-\dot{N}_A})_p\bar{P}_{pq}\epsilon_{pq}. \quad (27)$$

We introduce

$$\left.\begin{aligned}L_1&=\Sigma_r\Sigma_s\dot{N}_{Ar}R_{rs}\epsilon_{rs}/N_A,\\ \bar{L}_1&=\Sigma_r\Sigma_s\dot{N}_{Ar}\bar{R}_{rs}\epsilon_{rs}/N_A,\\ L_2&=\Sigma_p\Sigma_q(\overline{\dot{N}-\dot{N}_A})_pP_{pq}\epsilon_{pq}/N-N_A,\\ \bar{L}_2&=\Sigma_p\Sigma_q(\overline{\dot{N}-\dot{N}_A})_p\bar{P}_{pq}\epsilon_{pq}/N-N_A.\end{aligned}\right\} \quad (28)$$

Then

$$\begin{aligned}\Delta K = |\delta K|\,[&\omega_A[N_A^2 L_1+(N-N_A)N_A\bar{L}_1]\\ &+\omega_B[(N-N_A)^2 L_2+N_A[N-N_A]\bar{L}_2]\\ &-N_A^2[(L_1+L_2)-(\bar{L}_1+\bar{L}_2)]\\ &-NN_A[L_1+\bar{L}_2-2L_2]-N^2L_2 \quad . \quad (27.1)\\ = |\delta K|\,&(\omega_A\Phi_2+\omega_B\Phi_3-\Phi_1). \quad . \quad . \quad . \quad . \quad . \quad (27.2)\end{aligned}$$

The relation

$$\Phi_1 = \Phi_2+\Phi_3 \; . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27.3)$$

will frequently be made use of.

The equation for the variation in N_A becomes

$$\omega_A \underset{r}{\equiv} \frac{1}{j\nu\left(\dfrac{\dot{N}_{Ar}}{\dot{N}_{Ar}(N_A R_{rs}+(N-N_A)\bar{R}_{rs}-\dot{N}_{As}(N_A R_{sr}+(N-N_A)\bar{R}_{sr})}\right)+1} \quad . \quad . \quad . \quad (28)$$

ω_B is given by a similar equation.

The constants c_1, c_2, d_1, d_2 are defined as

$$c_1 = \left(R_{rs}-\frac{\dot{N}_{As}}{\dot{N}_{Ar}}R_{sr}\right),$$

$$c_2 = \left(\bar{R}_{rs}-\frac{\dot{N}_{As}}{\dot{N}_{Ar}}\bar{R}_{sr}\right),$$

$$d_1 = \left(P_{pq}-\frac{(\dot{N}-\dot{N}_A)_q}{(\dot{N}-\dot{N}_A)_p}P_{qp}\right),$$

$$d_2 = \left(\bar{P}_{pq}-\frac{(\dot{N}-\dot{N}_A)_q}{(\dot{N}-\dot{N}_A)_p}\bar{P}_{qp}\right).$$

Then

$$\omega_A = \frac{1}{j\nu\left[\dfrac{1}{c_1 N_A+c_2(N-N_A)}\right]+1} = \frac{1}{j\nu\vartheta_2+1}, \quad (28.1)$$

$$\omega_B = \frac{1}{j\nu\left[\dfrac{1}{d_1(N-N_A)+d_2 N_A}\right]+1} = \frac{1}{j\nu\vartheta_3+1}. \quad (28.2)$$

It is to be noticed that c_1 is a characteristic constant for the pure gas A, and is, in fact, precisely N/b_{A1}. Hence

$$c_1 = \frac{L_1}{\beta_A k}\frac{dK}{dT} \; . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Also

$$d_1 = \frac{L_2}{\beta_B k}\frac{dK}{dT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (29.1)$$

The assumptions of independence as regards r, of ω_A and c_1 (and ω_B and d_1), imply the constancy of c_2 (and d_2). We may, however, go further, *i. e.*,

$$c_2 \equiv_r \frac{(\dot{N}_{Ar}\bar{R}_{rs} - \dot{N}_{As}\bar{R}_{sr})\epsilon_r}{\dot{N}_{Ar}\epsilon_r}.$$

By composition we have, therefore,

$$c_2 = \frac{\sum_r \sum_s (\dot{N}_{Ar}\bar{R}_{rs} - \dot{N}_{As}\bar{R}_{sr})\epsilon_r}{\sum_r \dot{N}_{Ar}\epsilon_r}$$

$$= \frac{\sum_r \sum_s \dot{N}_{Ar}\bar{R}_{rs}\epsilon_{rs}}{\frac{d}{dK}\Sigma N_{Ar}\epsilon_r}$$

$$= \frac{\bar{L}_1 \frac{dK}{dT}}{\beta_A k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29.2)$$

Similarly,

$$d_2 = \frac{\bar{L}_2 \frac{dK}{dT}}{\beta_B k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29.3)$$

Except for the more involved expansion for ΔK, the energy transfer equation is the same as in Part I. With the aid of equations (26) it may be exhibited in the form :

$$j\nu N\left[\frac{3NV^2 - \frac{10}{3}SK}{3NV^2 - 2SK}\right] - \frac{\Phi_2}{j\nu\vartheta_2 + 1} - \frac{\Phi_3}{j\nu\vartheta_3 + 1} + \Phi_2 = 0. \quad (30)$$

On solving for $\frac{1}{V^2}$, the term independent of ν is seen to contain $\Phi_2 + \Phi_3 - \Phi_1$, and is therefore 0. To a first approximation we have, bearing in mind equation (27.3),

$$\frac{1}{V_0^2} = \frac{3N}{KS}\frac{N + (\vartheta_2\Phi_2 + \vartheta_3\Phi_3)}{\frac{10}{3}N + 2(\vartheta_2\Phi_2 + \vartheta_3\Phi_3)}. \quad . \quad . \quad (31)$$

Expanded, this is

$$\frac{1}{V_0^2} = \frac{3N\left[a\left(\frac{N_A}{N}\right)^3 + (b+c)\left(\frac{N_a}{N}\right)^2 + (d+e)\left(\frac{N_A}{N}\right) + (\bar{\beta}_B+1)L_2\bar{L}_1\right]}{KS\left[2a\left(\frac{N_A}{N}\right)^3 + (2b+\frac{10}{3}c)\left(\frac{N_A}{N}\right)^2 + (2d+\frac{10}{3}e)\frac{N_A}{N} + (2\bar{\beta}_B+\frac{10}{3})L_2\bar{L}_1\right]}, \quad \ldots \quad (31.1)$$

where

$$\bar{\beta} = \tfrac{2}{3}\beta$$

and

$$a = (L_1-\bar{L}_1)(\bar{L}_2-L_2)(\bar{\beta}_A-\bar{\beta}_B),$$

$$b = [L_2(L_1-\bar{L}_1)+\bar{L}_1(\bar{L}_2-L_2)]\bar{\beta}_A + [2L_2(\bar{L}_1-L_1)+\bar{L}_2(L_1-\bar{L}_1)+\bar{L}_1(L_2-\bar{L}_2)]\bar{\beta}_B,$$

$$c = (L_1-\bar{L}_1)(\bar{L}_2-L_2),$$

$$d = \bar{L}_1L_2\bar{\beta}_A+(L_2(L_1-3\bar{L}_1)+\bar{L}_2\bar{L}_1)\bar{\beta}_B,$$

$$e = L_2(L_1-\bar{L}_1)+\bar{L}_1(\bar{L}_2-L_2).$$

Two intermediate checks on the accuracy of the general expression for $\frac{1}{V_0^2}$ are obtained from the two limiting values for $N_A \to 0$ or $N_A \to N$. It is readily verified that these limiting values of equation (31.1) are precisely the La Place expressions for the velocity in gas A or B respectively.

We may point out here that in order to obtain the expansion for $\frac{1}{V_0^2}$ $\left(\text{and, in fact, for } \frac{1}{V^2}\right)$ in terms of $\frac{N_B}{N}$, it is only necessary to write N_B instead of N_A, and the subscript j for i, where $\begin{Bmatrix} i \\ j \end{Bmatrix} = 1, 2$ in equation (31.1)—hence entirely analogous simplifications in equation (31.1) may be made for very high or very low N_A concentrations.

We may remark the notable simplification of our formula

for molecules with no internal degrees of freedom (or at very low temperatures) for the velocity is then given by

$$\frac{1}{V_0} = \sqrt{\frac{3N}{KS}},$$

which seems quite plausible.

In theory all four parameters L_1, $\bar{L}_1$, L_2, $\bar{L}_2$ are obtainable from experimental data on the velocity variation with concentration. Of these, L_1 and L_2 are also involved separately in the two absorption coefficients for the pure gases. Equation (31.1) is, of course, rather unwieldy (even in the case $\beta_A = \beta_B$, for which the terms in the cubes of the concentrations drop out). The experimenter desiring to test the foregoing formulæ will see how to make the obvious simplifications at low and high concentrations (a real general simplification would depend on a closer study of the L's). We can say here, as regards their order of magnitude, that a rough estimate would be $\frac{10^{-7}}{N}$ for strong to about $\frac{10^{-9}}{N}$ for weak absorption.

In order to determine the absorption in the general case, it is necessary to write down the complete expression for $\frac{1}{V^2}$. Reference to equation (30) yields

$$\frac{1}{V^2} = \frac{3N}{KS} \frac{\begin{matrix}[N + (\vartheta_2\phi_2 + \vartheta_3\phi_3) + j\nu\,[(\vartheta_2 + \vartheta_3)N + \phi_1\vartheta_2\vartheta_3] \\ -\nu^2\vartheta_2\vartheta_3 N\end{matrix}}{\begin{matrix}\frac{10}{3}N + 2(\vartheta_2\phi_2 + \vartheta_3\phi_3) + \nu\left[\frac{10}{3}(\vartheta_2 + \vartheta_3)N + 2\phi_1\vartheta_2\vartheta_3\right] \\ -\frac{10}{3}N\nu^2\vartheta_2\vartheta_3\end{matrix}}, \quad \ldots \quad (32)$$

or

$$\frac{1}{V} = \frac{1}{V_0}\left[1 - \frac{j\nu N(\vartheta_3^2\phi_3 + \vartheta_2^2\phi_2)}{5N^2 + 8N(\vartheta_3\phi_3 + \vartheta_2\phi_2) + 3(\vartheta_2\phi_2 + \vartheta_3\phi_3)} + \cdots\right], \quad \ldots \quad (33)$$

where it is to be noticed that V_0, also, involves N_A. The expanded form for the imaginary part * of $\frac{1}{V}$ evidently reduces to the quotient of a 4th-degree by a 6th degree polynomial in N_A. The complete expansion may be supplied

* We may, of course, easily calculate the value of the diminution in amplitude, but the result is hardly verifiable.

by the reader. If we confine ourselves to very small N_A concentrations (a similar expansion is true for N_A large, *cf. supra*) and retain terms up to the 2nd degree only, we have for the numerator

$$\frac{N_A^2}{N^2}\{[L_2^2[L_1-\bar{L}_1]+2L_1[\bar{L}_2-L_2]L_2]\bar{\beta}_A^2 + [(L_2-\bar{L}_2)\bar{L}_1^2+2(\bar{L}^2-2L_2)(L_1-\bar{L}_1)\bar{L}_1 + L_2(L_1-\bar{L}_1)^2]\bar{\beta}_B^2\} + \frac{N_A}{N}\{[L_2^2\bar{L}_1\bar{\beta}_A^2+[(\bar{L}_2-2L_2)\bar{L}_1^2+2L_2(L_1-\bar{L}_1)\bar{L}_1]\bar{\beta}_B^2 + \bar{\beta}_B^2L_2\bar{L}_1^2\}.$$

The denominator is the product of the numerator and denominators of the fraction in equation (31.1), exclusive of the factor $\frac{3N}{KS}$.

It may be pointed out that the assumption $L_i=\bar{L}_i$ would be tantamount to considering the mixture to be a single gas for which the parameters $\frac{\beta^2}{L}$ and β were the means of the values for the components.

Abello * measured the ratio of the absorption in air to that of air mixed with another gas. On our theory it is clear that the ratio of the transmitted intensities is e raised to the quotient of two 6th-degree polynomials † in the concentrations ‡. For the special case that $L_i=\bar{L}_i$ we write the ratio of the transmissions as

$$\frac{I_{mixture}}{I_{air}} = \exp-\frac{8\pi^2\nu^2 r\left[g_1\left(\frac{N_A}{N}\right)^2+g_2\left(\frac{N_A}{N}\right)+g_3\right]}{\left\{g_4\left(\frac{N_A}{N}\right)^2+g_5\left(\frac{N_A}{N}\right)+g_6\right\}NV_mV_A},$$

where the subscript A refers to air, and

$$g_1=-\frac{16}{27}\frac{\beta_B^2}{L_2}(\beta_A-\beta_B)^2,$$

$$g_2=\frac{4}{3}\left\{\frac{\beta_A^2}{L_1}\bar{H}V-\frac{\beta_B^2}{L_2}\left(\bar{H}V + \left[\frac{16}{3}(\beta_A-\beta_B)+\frac{8\beta_B}{3}(\beta_A-\beta_B)\right]V_m\right)\right\},$$

* T. P. Abello, Proc. Nat. Acad. xiii. p. 699 (1927); Phys. Rev. June 1926, p. 1083.

† Assuming for the moment that air is a single gas.

‡ Exclusive of the dependence of S on N_A.

$$g_3 = \frac{4}{9}\bar{H}\frac{\beta_B^2}{L_2}(V - V_m),$$

$$g_4 = \frac{4}{3}(\beta_A - \beta_B)^2,$$

$$g_5 = \frac{16}{3}(\beta_A - \beta_B) + \frac{8}{3}\beta_B(\beta_A - \beta_B),$$

$$g_6 = \bar{H} = \left(5 + \frac{16}{3}\beta_B + \frac{4}{3}\beta_B^2\right),$$

V = sound velocity in air,

V_m = sound velocity in the mixture.

For the case $\beta_A = \beta_B$ this reduces still further; thus

$$\frac{I_{mixture}}{I_{air}} = \exp - \frac{8\pi^2\nu^2\left[\frac{4}{3}V\left(\frac{\beta_A^2}{L_1} - \frac{\beta_B^2}{L_2}\right)\frac{N_A}{N} + \frac{4}{9}\frac{\beta_B^2}{L^2}(V - V_m)\right]}{N V_m V}.$$

Abello's empirical conclusion was that the logarithm of the ratio of the transmissions is a linear function of the concentration. It does not seem from our results that this can be true in general; and, even in the most favourable case, namely that in which the gases dealt with are properly characterized by the assumption $L_i = \bar{L}_i$, we should expect ordinarily the ratio of two quadratics in the concentrations *. Abello's relation holds in this extreme case only when the number of degrees of freedom of the component gases are the same and $\frac{1}{m_A}$ is not very different from $\frac{1}{m_B}$.

A number of topics for experimental study are suggested by the foregoing analysis, the details of which may be easily extended to the general case of mixtures of n gases.

Appendix.

To derive equation (11) we proceed as follows:—

Equation (3.2) may be written in the form

$$\omega_r - \lambda N \Sigma\left(R_{rs}\omega_r - \frac{\dot{N}_s}{\dot{N}_r}R_{sr}\omega_s\right) = -\lambda N\frac{A_r}{\dot{N}_r},$$

where $\lambda = \frac{j}{\nu}$.

* Exclusive of the dependence of S on N_A.

On solving for ω_m, the denominator determinant is seen to be of the form

$$\begin{vmatrix} 1-\lambda N\sum_s R_{1s} & \lambda\frac{\dot{N}_2}{\dot{N}_1}R_{21}\ldots & \lambda\frac{\dot{N}_n}{\dot{N}_1}R_{n1} \\ \lambda\frac{\dot{N}_1}{\dot{N}_n}R_{1n} & & 1-\lambda N\sum_s R_{ns} \end{vmatrix} = \Delta.$$

On expanding the determinant in powers of λ, it is evident that we have

$$\Delta = 1-\lambda N\sum_s\sum_r R_{sr}+\ldots.$$

The numerator takes the form

$$\sum_s -\lambda A_s\dot{N}\Delta_{ms}/\dot{N}_s,$$

where Δ_{ms} is the co-factor of the term in the mth column and sth row of Δ. For $m\neq s$ it will be seen that

$$\Delta_{ms} = -\lambda R_{sm}\frac{N\dot{N}_s}{\dot{N}_m}.$$

Except for the absence of the mth column and mth row, Δ_{mm} is of the same type as Δ; hence

$$\Delta_{mn} = 1-\lambda N\sum_s\sum_r(R_{sr}-R_{mr})+\ldots.$$

Accordingly

$$\omega_m = \frac{\lambda^2 N\sum_s{}^*\frac{A_s N}{\dot{N}_s}\left(\frac{R_{sm}\dot{N}_s}{\dot{N}_m}\right)-\lambda\frac{A_m N}{\dot{N}_m}\left[1-\lambda N\sum_s\sum_r(R_{sr}-R_{mr})\right.}{1-N\lambda\sum_s\sum_r R_{sr}},$$

where Σ^* indicates that the term $s=m$ is omitted. It is, however, clear that since $R_{mm}=0$, we may replace Σ^* by the general summation symbol over all s.

On writing

$$\frac{1}{1-N\lambda\sum_s\sum_r R_{sr}} = 1+N\lambda\sum_s\sum_r R_{sr}+\lambda^2,$$

we obtain, after evident reductions, equation (11).

A check on the accuracy of equation (11) is afforded if it be assumed that $\frac{A_s}{\dot{N}_s}$ is independent of s. It is clear that we should find

$$\omega = -\lambda \frac{A_m N}{\dot{N}_m} - \lambda^2 \frac{A_s N}{\dot{N}_s} \sum_s \frac{A_{sm} \dot{N}_s}{\dot{N}_m} A_{ms}$$

or

$$-\lambda \frac{A_m N}{\dot{N}_m} + \lambda^2 \left(\frac{A_m N}{\dot{N}_m} \right)^2$$

in agreement with equation (22).

XCVIII. *The Absorption of High-Frequency Radiation.* By Edmund C. Stoner, *Ph.D.* (*Cambridge*), *Reader in Physics, University of Leeds* *.

Introduction.

A NUMBER of formulæ have been put forward for the variation with wave-length of the absorption coefficient of high-frequency radiation. Before any of these formulæ can be applied with confidence, it is necessary to consider how far they are in agreement with experimental results on absorption. A simple direct comparison of theory and experiment is not at present possible, for the γ radiation, which is amenable to accurate experimental investigation, is heterogeneous. It is only for the γ-rays of RaB and C that data which are at all satisfactory are available for the intensity distribution, as well as for the wave-lengths; with these data, together with those on the mean absorption coefficient, it is possible to make a decision as to which of the absorption formulæ is in best agreement with experiment. It is perhaps premature to make this comparison, owing to the lack of finality in connexion with the intensity distribution; but it seems desirable to make a preliminary investigation, particularly in view of the fact that various formulæ have been used in deducing the wave-lengths of cosmic rays without any adequate ground for the view that they hold good even for the longer γ-rays. In this paper the intensity distribution given by Ellis will be modified in the light of his later work. Using different absorption formulæ, a calculation will then be made as to the mean

* Communicated by Prof. R. Whiddington, F.R.S.

absorption coefficient which would be deduced from experiments such as those of Ahmad, and the results compared with those he obtained. It will be seen that the experimental results are consistent with the Klein-Nishina relativistic formula, but not with the unmodified Dirac formula. This has an important bearing on the interpretation of the cosmic ray absorption results.

The Intensity Distribution of γ*-rays of* RaB *and* RaC.

An estimate of the intensities of the γ-rays from RaB and C has been made by Ellis and Wooster *. The method followed will be briefly indicated.

Let $V_1, V_2, V_3 \ldots V_n$ be the energies (proportional to the frequencies) expressed in volts of the γ-rays emitted; and let $p_1, p_2, p_3 \ldots p_n$ be the probabilities of emission, so that in N disintegrations there are emitted $Np_1, Np_2 \ldots Np_n$ γ-rays of energies $V_1, V_2 \ldots V_n$. For a γ-ray V_r, let ${}_K\alpha_r$ be the probability of internal conversion in the K level. Let $p_r\,{}_K\alpha_r = \theta_r$. Then, in N disintegrations, the number of electrons ejected from the K level by internal conversion of the γ-ray V_r is equal to $N\theta_r$. Now ${}_K\alpha_r$ will vary with the frequency of the γ-ray. Let g be the value for a standard γ-ray ($V = 3{\cdot}54 \times 10^5$ volts is taken), and for any γ-ray write

$$ {}_K\alpha_r = gf(V_r), $$

where

$$ f(V_r) = 1 \quad \text{for} \quad V = 3{\cdot}54 \times 10^5 \text{ volts}. $$

The probability of absorption in the L, M ... levels, taken together, is approximately ·22 of that of absorption in the K level. Thus the total energy emitted from the atom, per disintegration, in the form of γ-rays (which have not been internally converted) is given by

$$ \begin{aligned} E &= \sum_1^n p_r V_r (1 - 1{\cdot}22\,{}_K\alpha_r) \\ &= \sum_1^n \left[\frac{\theta_r V_r}{gf(V_r)} - 1{\cdot}22\,\theta_r V_r \right] \end{aligned} $$

Ellis and Wooster consider 7 γ-rays from RaB ($V_1, V_2 \ldots V_7$) and 7 from RaC ($V_8, V_9 \ldots V_{14}$). In analogy with the external absorption coefficient, the internal absorption coefficient was taken to be slightly greater for RaC than RaB.

$$ g_{\text{RaC}} = 1{\cdot}03\, g_{\text{RaB}}. $$

* C. D. Ellis and W. A. Wooster, Proc. Camb. Phil. Soc. xxiii. p. 717 (1927).

It was also assumed that the internal absorption coefficient varied continuously as some power of the wave-length (or as some inverse power of V). Using the values of θ_r which may be deduced from the measurements on the β-ray group intensities, various powers of V are tried to see which gives results in closest agreement with the observed heating effect of the γ-rays (Ellis and Wooster *) and the observed number of γ-ray impulses (Kovarik †).

Let E be the γ-ray energy in the disintegration of 1 atom of RaB and 1 atom of RaC, and N the total number of impulses. The experimental data ‡ are as follows:—

$E = 18{\cdot}4 \times 10^5$ volts, $E_{RaB} = 1{\cdot}44 \times 10^5$, $E_{RaC} = 16{\cdot}96 \times 10^5$, $N = 2{\cdot}14$, $N_{RaB} = {\cdot}51$, $N_{RaC} = 1{\cdot}63$.

For the total number of impulses

$$N = \sum_1^7 \frac{\theta_r}{gf(V_r)} + \frac{1}{1{\cdot}03} \sum_8^{14} \frac{\theta_r}{gf(V_r)} - 1{\cdot}22 \Sigma \theta_r ;$$

while for the total energy

$$E = \sum_1^7 \frac{\theta_r V_r}{gf(V_r)} + \frac{1}{1{\cdot}03} \sum_8^{14} \frac{\theta_r V_r}{gf(V_r)} - 1{\cdot}22 \Sigma \theta_r V_r^2 .$$

It is convenient to consider the values for RaB and RaC separately, as this gives a more definite criterion in subsequent tests of the absorption formulæ tried; for the whole process essentially reduces to an estimation of the relative intensities of the high and low frequency components of the radiation. Inserting the numerical values given, the following four equations are then obtained:—

$$\text{Energy} \ldots\ldots \begin{cases} \sum_1^7 \frac{\theta_r V_r}{f(V_r)} = 2{\cdot}05\, g, \ldots (1) \\ \sum_8^{14} \frac{\theta_r V_r}{f(V_r)} = 17{\cdot}51\, g ; \ldots (2) \end{cases}$$

$$\text{Impulses} \ldots\ldots \begin{cases} \sum_1^7 \frac{\theta_r}{f(V_r)} = {\cdot}68\, g, \ldots (3) \\ \sum_8^{14} \frac{\theta_r}{f(V_r)} = 1{\cdot}69\, g. \ldots (4) \end{cases}$$

* C. D. Ellis and W. A. Wooster, Phil. Mag. l. p. 521 (1925).

† A. F. Kovarik, Phys. Rev. xxiii. p. 559 (1924).

‡ The number of atoms disintegrating per second from 1 mg. is taken as $3{\cdot}4 \times 10^7$. The later result—$3{\cdot}68 \times 10^7$ (H. J. J. Braddick and H. M. Cave, P. R. S. cxxi. p. 367 (1928))—would reduce the value of g and the absolute intensities (Table III.) by a factor $3{\cdot}4/3{\cdot}68 = {\cdot}92$, but would not affect the relative intensities calculated.

In Table I. are given the values of λ, V, and θ for the 14 γ-rays considered. The values of θ (the intensities of the β-ray group due to K conversion of the γ-ray) for the RaC rays differ from those given by Ellis *, having been corrected in the light of later work by him and Aston † on the photographic action of β-rays.

TABLE I.

γ-ray Energies and β-ray Intensities.

	Number of γ-ray.	λ, 10^{-11} cm.	Energy, 10^5 volts,	θ.
RaB.	1	50·5	2·43	·0314
	2	47·3	2·60	·0038
	3	44·5	2·76	·0019
	4	41·6	2·97	·0435
	5	34·7	3·54	·0550
	6	26·2	4·71	·0008
	7	25·5	4·82	·0008
RaC.	8	20·1	6·12	·00380
	9	13·3	9·41	·00052
	10	10·9	11·30	·00132
	11	9·87	12·48	·00058
	12	8·62	14·26	·00318
	13	6·92	17·78	·00073
	14	5·55	22·19	·00018

For various assumed rates of variation of the absorption coefficient with the wave-length, values of g can be calculated from equations (1)–(4). The correct formula for $f(V)$ should give the same value of g in all four cases, provided the experimental results are correct. Dr. Ellis has kindly informed me that his later experimental results show that the variation with wave-length, as tested by a comparison of the internal with the external absorption, shows marked divergencies from continuity for the γ-rays 6·12 and $14{\cdot}26 \times 10^5$ volts. Although, in general, the internal absorption may be approximately represented by the formula $f(V)=V^{-x}$, for the 6·12 ray the absorption is about three times as small as this, and for the 14·26 about

* C. D. Ellis and W. A. Wooster, Proc. Camb. Phil. Soc. xxiii. p. 717 (table i. p. 723) (1928).

† C. D. Ellis and G. H. Aston, Proc. Roy. Soc. cxix. p. 645 (1928).

three times as great. Calculations of the value of g have been made, therefore, using the formulæ

$$f(V) = \left(\frac{V}{3{\cdot}54}\right)^{-x} \quad \text{for all } \gamma\text{-rays except 8 and 12,}$$

$$f(V_8) = \frac{1}{3}\left(\frac{V}{3{\cdot}54}\right)^{-x},$$

$$f(V_{12}) = 3\left(\frac{V}{3{\cdot}54}\right)^{-x}.$$

The values of x tried were 2·5, 2·6, and 2·7.
The results are shown in Table II.

TABLE II.

Calculated Values of g.

		$V^{-2\cdot5}$.	$V^{-2\cdot6}$.	$V^{-2\cdot7}$.
Energy	RaB (1)	·160	·159	·158
	RaC (2)	·138	·159	·180
Impulses	RaB (3)	·148	·147	·146
	RaC (4)	·111	·123	·136

If the estimate of the division of energy between the γ-rays of RaB and RaC is approximately correct (Ellis and Wooster consider it is probably correct to 10 per cent.), the above figures indicate fairly definitely a rate of variation of absorption varying as $V^{-2\cdot6}$. The results of the heating experiments, however, are not consistent with those of the counting experiments. The counting experiments, taken alone, would indicate a power considerably greater than 2·7 ; while if the results from the total number of impulses (RaB and C) are compared with the total heating effect, a power considerably less than 2·5 would be indicated—a result at variance with the ratio of the effects of RaB to RaC either in the counting or heating experiments.

On the whole, it seems that the heating experiments are less liable to give spurious results than the counting. If it is assumed that the internal absorption coefficient is equal to $\cdot159\left(\frac{V}{3{\cdot}54}\right)^{-2\cdot6}$ in accordance with the heating results, the lower value of g for that power of V deduced from the number of impulses, indicates that the number of impulses counted is larger than the number of γ-ray quanta emitted from the atom; moreover, that the excess is greater

in the case of the hard γ-rays from RaC than the softer rays from RaB. This is precisely what might be expected, if, as has been suggested, a high-speed photoelectron may give rise, by collision, to another fast electron. If the value ·159 for g is correct, the number of primary impulses (which actually escape from the atom) per disintegrating atom would be given by

$$N_{RaB} = \frac{\cdot 147}{\cdot 159} \times \cdot 51 = \cdot 47 \quad \text{(Observed } \cdot 51\text{)},$$

$$N_{RaC} = \frac{\cdot 123}{\cdot 159} \times 1\cdot 63 = 1\cdot 26 \quad \text{(Observed } 1\cdot 63\text{)}.$$

In view of the uncertainties in the counting experiments, the general run of the internal absorption coefficient will be taken to be given approximately by the formula

$$\cdot 159\left(\frac{V}{3\cdot 54}\right)^{-2\cdot 6}$$

with the exceptions above mentioned for the lines $V = 6\cdot 12$ and $V = 14\cdot 26 \times 10^5$ volts. The values of p_r, the number of γ-rays per disintegration, and of $p_r V_r$, which is proportional to the intensity of the γ-rays, can then be calculated. These values, which are required for the calculation of the mean absorption coefficients, are given in Table III.

The Absorption of γ-Rays.

The absorption of the γ-rays from RaB and C has been comprehensively and carefully investigated by Ahmad*, whose results will here be considered. He found that the absorption per atom of the heterogeneous rays could be expressed by the formula

$$\mu_A = aZ + bZ^4,$$

where Z is the atomic number.

The first term was taken to be associated with scattering absorption, the second with photoelectric absorption. By assuming that b has the value that holds approximately in the X-ray region ($3\cdot 29 \times 10^{-2}\lambda^3$) and that a was given by the Compton formula, the two values deduced for the "mean effective wave-length" were found to be in rough agreement. But it was pointed out that this was partly fortuitous, and

* N. Ahmad, P. R. S. c. p. 507 (1924); cix. p. 206 (1925); (and E. C. Stoner) cvi. p. 8 (1924).

it was concluded "that the wave-length as estimated from the scattering absorption by the Compton formula is too great." The essential value of Ahmad's work, however, was not due to its leading to a rough estimate of a mean wave-length, but to its showing that the absorption of γ-rays could be attributed to two distinct processes (as in the case of X-rays) and to its providing accurate data for the absorption coefficients under well-defined conditions.

TABLE III.

Calculated Intensities of γ-Rays from RaB and RaC.

	Number of γ-ray.	λ 10^{-1} cm.	p_r, No. of quanta per disintegration.	$p_r V_r$, 10^5 volts.
RaB.	1	50·5	·073	·178
	2	47·3	·011	·028
	3	44·5	·006	·017
	4	41·6	·173	·510
	5	34·7	·346	1·213
	6	26·2	·011	·052
	7	25·5	·012	·058
			$\sum_1^7 p_r$ ·632	$\sum_1^7 p_r V_r$ 2·056
RaC.	8	20·2	·295	1·81
	9	13·3	·044	·41
	10	10·9	·173	1·85
	11	9·87	·096	1·20
	12	8·62	·247	3·52
	13	6·92	·305	5·42
	14	5·55	·142	3·15
			$\sum_8^{14} p_r$ 1·302	$\sum_8^{14} p_r V_r$ 17·46

It will be most convenient for the present purpose to consider Ahmad's values for the scattering absorption per electron, σ. The final results for σ/σ_0 ($\sigma_0 = 6{\cdot}64 \times 10^{-25}$, the classical value) after filtering the rays, are shown in Table IV.

The above values include a correction of about 10 per cent. for the rays scattered forward into the ionization chamber. This correction is calculated from the estimated mean wave-length; but this means, effectively, that it is calculated so

as to be consistent with the directly observed absorption, and it will not be greatly in error even if an incorrect scattering formula is used; so that the error introduced into the final value for the scattering will be very small.

TABLE IV.

Scattering per Electron for γ-Rays from RaB and C.

Filter.	σ/σ_0.
·5 cm. Fe	·327
2·5 cm. Fe	·315
6·5 cm. Fe	·312
1·0 cm. Pb	·298
3·4 cm. Hg	·297

The values obtained depend, of course, on the experimental arrangements—in particular, on the form of the ionization chamber used. This has long been recognized, but the problem, if attacked directly, becomes very complicated. A simple method will be given later by which a general idea may be obtained as to how far the deduced absorption coefficients are influenced by the ionization chamber factor.

Absorption Formulæ.

The scattering absorption formula made use of by Ahmad was that of Compton *.

$$\frac{\sigma}{\sigma_0} = \frac{1}{1+2\alpha},$$

$$\sigma_0 = 6{\cdot}64 \times 10^{-25},$$

$$\sigma = \frac{h\nu}{mc^2} = \frac{{\cdot}0242}{\lambda}.$$

For this formula there was little theoretical justification, but it was useful as an empirical expression of the general nature of the variation of the scattering with wave-length.

On the basis of the quantum mechanics, Dirac † has given the formula:

$$\frac{\sigma}{\sigma_0} = \frac{3}{4}\frac{1+\alpha}{\alpha^2}\left\{\frac{2(1+\alpha)}{1+2\alpha} - \frac{1}{\alpha}\log(1+2\alpha)\right\} \quad . \quad . \quad (5)$$

* A. H. Compton, Phys. Rev. xxi. p. 483 (1923).
† P. A. M. Dirac, Proc. Roy. Soc. A, cxi. p. 423 (1926).

Klein and Nishina * have pointed out that Dirac's relativistic theory of the electron necessitates a modification of this formula (owing to the introduction of terms with $\left(\frac{h\nu}{mc^2}\right)^2$ in the formula connecting scattering with angle), and they give for the total scattering absorption:

$$\frac{\sigma}{\sigma_0}=\frac{3}{4}\left[\frac{1+\alpha}{\alpha^2}\left\{\frac{2(1+\alpha)}{1+2\alpha}-\frac{1}{\alpha}\log(1+2\alpha)\right\}+\frac{1}{2\alpha}\log(1+2\alpha)-\frac{1+3\alpha}{(1+2\alpha)^2}\right]. \quad (6)$$

The difference in the numerical values given by these formulæ is illustrated by the figures in Table V. for wave-lengths in the range being considered.

TABLE V.

Scattering Absorption per Electron, σ/σ_0.

C, Compton; D, Dirac; K-N, Klein and Nishina.

λ, 10^{-11} cm.	α.	C.	D.	K-N.
48·4	·5	·50	·51	·56
24·2	1	·33	·35	·43
12·1	2	·20	·22	·34
6·0	4	·11	·13	·23

For homogeneous rays with the coefficient ·327 found by Ahmad, the three formulæ would give wave-lengths of about 23·6, 21·5, and $11{\cdot}0\times10^{-11}$ cm. Calculation of the "mean wave-length" from Table V. ($\overline{\lambda}=\Sigma p_r V_r \lambda_r/\Sigma p_r V_r$) gives a value of about 12×10^{-11} cm., which suggests that the Klein-Nishina formula is in closest agreement with the experimental results. But it is not legitimate to base any conclusions on this rough indication. The test of the Dirac and Klein-Nishina formulæ will now be considered in greater detail.

Test of Absorption Formulæ.

The question to be considered is the relation between the mean absorption coefficient for a heterogeneous beam found experimentally, and the absorption coefficients of the homogeneous constituents.

* O. Klein and Y. Nishina, 'Nature,' cxxii. p. 398 (1928).

Let I_0 be the initial intensity of the beam.

$$I_0 = I_1 + I_2 \ldots + I_r + \ldots = \Sigma I_q.$$

If the absorber is not too thick—in Ahmad's experiments the thickness was chosen so that about 20 per cent. of the radiation was absorbed—the decrease in intensity in passing through a thickness δx is given by

$$\delta I_0 = \bar{\mu} I_0 \, \delta x = (\Sigma \mu_r I_r) \, \delta x.$$

If the ionization chamber absorbs all the radiation completely in such a way that the ionization current is directly proportional to the intensity of the radiation, the ordinary mean absorption coefficient will be deduced from the experiments.

$$\mu = \frac{\Sigma \mu_r I_r}{\Sigma I_r} = \frac{\Sigma \mu_r I_r}{I_0}.$$

Ahmad's experiments enabled the scattering absorption coefficient to be separated from the photoelectric absorption coefficient. The value of the scattering coefficient per electron $(\bar{\sigma})_1$, which would be deduced if the above conditions held, is given by

$$(\bar{\sigma})_1 = \frac{\Sigma I_r \sigma_r}{I_0}.$$

Since I_r is proportional to $p_r V_r$ (see Table V.), this may be written :

$$\overline{\left(\frac{\sigma}{\sigma_0}\right)}_1 = \Sigma p_r V_r \left(\frac{\sigma}{\sigma_0}\right)_r \Big/ \Sigma p_r V_r \ldots \quad (7)$$

This expression gives a limiting value which would be deduced if the ideal conditions could be realized.

Now, suppose that the ionization chamber absorbs only a fraction of the incident radiation, and, as before, that the ionization current is proportional to the amount absorbed. Let l be the length of the chamber, μ_r' the absorption coefficient for the rth constituent of the radiation. The initial intensity, I_0', then measured would be

$$I_0' = \Sigma I_r (1 - e^{-\mu_r' l}).$$

The measured absorption coefficient (of the absorber) would be given by

$$\bar{\mu} = \frac{1}{I_0'} \frac{\delta I_0'}{\delta x}$$

$$= \Sigma \mu_r I_r (1 - e^{-\mu_r' l}) / \Sigma I_r (1 - e^{-\mu_r'' l}).$$

In the limiting case, when $\mu' l$ is small, this gives

$$\bar{\mu} = \Sigma \mu_r \mu_r' \mathrm{I}_r / \Sigma \mu_r' \mathrm{I}_r.$$

For the scattering absorption per electron,

$$\overline{\left(\frac{\sigma}{\sigma_0}\right)}_2 = \Sigma p_r \mathrm{V}_r \left(\frac{\sigma}{\sigma_0}\right)_r \mu_r' / \Sigma p_r \mathrm{V}_r \mu_r' . \quad . \quad . \quad . \quad (8)$$

This gives a second limiting case.

The conditions necessary for the application of either of these equations are not satisfied, but are intermediate.

In Ahmad's later experiments the ionization chamber was about 15 cm. long, and contained lead plates of aggregate thickness 1·05 cm. His experiments show that there is about 54 per cent. absorption of the radiation in passing through 1 cm. of lead. While the longer wave-length radiation is almost completely absorbed, probably only about 20 per cent. of the shortest wave-length radiation will be. As far as the absorption in the ionization chamber is concerned, therefore, the conditions are intermediate between those required for equations (7) and (8).

A difficulty arises in that whereas the ionization current in a gas (due almost entirely to the recoil electrons produced in the Compton scattering process) may be taken as proportional to the absorption, much of the absorption in the lead plates gives rise to no ionization current, but simply results in heating. The question is of importance in the choice of the best value of μ' in equation (8). The values of μ' are proportional to the absorptions per electron, and if these were the same for air and lead, the question of choice would not arise. But for lead an appreciable part of the absorption for the long wave-lengths is due to photoelectric absorption; only a fraction of this, however, will add to the ionization current; so that the calculations will be made using (*a*) μ_e for air, (*b*) μ_e for lead.

The value of μ_e is given by

$$\mu_e = \sigma + \tau.$$

σ may be calculated for different wave-lengths, using the Dirac, or Klein-Nishina, formula. τ will be taken as

$$\tau = 2{\cdot}29 \times 10^{-2} \lambda^3 \mathrm{Z}^3.$$

This is, of course, an extrapolation from the X-ray results, and is probably sufficiently correct for the present purpose.

In Table VI. are given the values which would be deduced for the mean (σ/σ_0) for a heterogeneous beam with the

intensity distribution of Table V., using the Dirac and Klein-Nishina formula. The values are calculated from the following formulæ :—

$$(\sigma/\sigma_0)_1 = \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)\Big/\Sigma I_r, \quad \ldots\ldots\ldots \quad (7)$$

$$(\sigma/\sigma_0)_{2a} = \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)\mu'_{ar}\Big/\Sigma I_r\mu'_{ar}, \quad \text{where } \mu'_a = \mu_{\text{air}},$$

$$= \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)^2\Big/\Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right), \quad \ldots\ldots \quad (8\,a)$$

$$(\sigma/\sigma_0)_{2b} = \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)\mu'_{br}\Big/\Sigma I_r\mu'_{br}, \quad \text{where } \mu_b = \mu_{\text{Pb}},$$

$$= \Sigma I_r\left(\frac{\sigma_r}{\sigma_0}\right)\left(\frac{\mu_e}{\sigma_0}\right)_{\text{Pb}r}\Big/\Sigma I_r\left(\frac{\mu_e}{\sigma_0}\right)_{\text{Pb}r} \quad \ldots \quad (8\,b)$$

TABLE VI.

Calculated and Observed Mean Absorption Coefficients.

	Dirac (5).	Klein-Nishina (6).
$(\sigma/\sigma_0)_1$ from (7)	·203	·308
$(\sigma/\sigma_0)_{2a}$ from (8 *a*)	·253	·331
$(\sigma/\sigma_0)_{2b}$ from (8 *b*)	·325	·382
$(\sigma/\sigma_0)_2$ Mean	·289	·356
Mean $\frac{1}{2}(\sigma/\sigma_0)_1+\frac{1}{2}(\sigma/\sigma_0)_2$.....	·246	·332
Observed	·327	

The observed value tabulated is that obtained after the rays had been filtered through ·5 cm. iron. Without filtering, rough extrapolation indicates that the observed value would be about 2 per cent. higher than this. The mean value calculated using the Klein-Nishina formula agrees remarkably well with that observed. The observed value is incompatible with the unmodified Dirac formula.

Effect of Filters.

As the absorption in the ionization chamber of the unfiltered rays is about 50 per cent., the method of calculating a mean value as above seems justifiable, but it would be expected that, as the rays are progressively hardened by filters, the observed absorption would tend towards the value

calculated using (8) rather than (7). Some calculations were therefore made as to the mean absorption coefficients which would be deduced after the rays had been filtered through ·5, 1·5, and 6·5 cm. iron, 1 cm. lead, and 3·41 cm. mercury, as in Ahmad's experiments. The intensity of a ray after passing through a thickness x of a substance is given by

$$I_r = (I_r)_0 \, e^{-\mu_r x}.$$

Let μ_e be the absorption coefficient per electron.

$$\mu = \frac{N\rho}{A} Z\mu_e$$

where Z = atomic number, ρ = density,
A = atomic weight, $N = 6{\cdot}06 \times 10^{23}$
$\mu_e = \sigma + \tau = \sigma + 2{\cdot}29 \times 10^{-5}\lambda^3 Z^3$.

The intensity of each of the rays was calculated using the Klein-Nishina formula for σ, and the mean values of the absorption coefficients after filtration estimated as before. The results are shown in Table VII.

As the beam is progressively filtered, owing to the variation in the absorption coefficient with wave-length, there will be an increase in homogeneity. and the beam will

TABLE VII.

Calculated and Observed Values of $(\sigma/\sigma_0) \times 10^3$.

Filter.	—	0·5 cm. Fe.	2·5 cm. Fe.	6·5 cm. Fe.	1 cm. Pb.	3·41 cm. Hg.
$(\sigma/\sigma_0)_1$ from (7)	308	300	281	260	276	260
$(\sigma/\sigma_0)_{2a}$ from (8 *a*)	331	324	301	272	286	265
$(\sigma/\sigma_0)_{2b}$ from (8 *b*)	382	364	326	285	300	265
$(\sigma/\sigma_0)_2$ Mean	356	344	313	278	292	265
Mean $\frac{1}{2}(\sigma/\sigma_0)_1 + \frac{1}{2}(\sigma/\sigma_0)_2$ ...	332	322	297	269	284	262
Observed	(333)	327	315	312	298	207

eventually be composed mainly of only the shortest wave-length radiations of those initially present (see Table V.). For the three shortest—$\lambda = 8{\cdot}62$, $6{\cdot}92$, $5{\cdot}55$—the values for (σ/σ_0) are ·286, ·250, and ·216 ; so the values calculated for the beam after filtration through 6·5 cm. iron and 3·41 cm. mercury (·269 and ·262) are of the order of magnitude to be expected. It would be expected, then, that as the filters

increase in thickness, the measured value of (σ/σ_0) would tend to a limiting value, and that this would agree more closely with that calculated from equation (8), corresponding to partial absorption in the ionization chamber, than from equation (7), corresponding to complete absorption. This tendency to a limit is observed with iron, the value with 6·5 cm. (·312) being only slightly less than with 2·5 cm. (·315); and also when 3·41 cm. mercury is substituted for 1 cm. lead (·297 and ·298). But the numerical values observed with thick filters are much greater than those calculated. The calculated "hardening effect" of the lead filter is actually less than that of the thick iron filter, and that of the mercury only slightly greater; while the observed hardening of the lead and mercury, though less than that calculated, is much greater than that of iron.

No obvious explanation of these discrepancies suggests itself. If the absorption coefficient for the shorter wave-lengths was greater than that calculated from the Klein-Nishina formula, some of the discrepancies would be removed, but the difference in the observed effect of mercury and iron would still be unexplained. It may be that, owing to the scattered radiation being concentrated in a forward direction, a certain amount of scattered radiation accompanies the beam, so that its effective mean wave-length, and scattering coefficient, is greater than that calculated; and that then the photoelectric absorption in lead and mercury, owing to its more rapid variation with wave-length, accounts for the increased hardening effect of these elements. (The value of τ/σ for lead varies from about $\frac{1}{8}$ to $\frac{1}{70}$ as λ varies from 13·3 to 5·5). It does not, however, seem desirable to speculate too much until the intensity distribution of the γ-rays is known with greater certainty.

In Ahmad's experiments a strictly parallel beam was not used, and as it is a matter of some difficulty to correct for scattering, it seems not improbable that scattering effects may play a rôle in the manner suggested. In some experiments by Kohlrausch *, a parallel beam was used, and the results were analysed so that effectively the final values corresponded to rays filtered through 4 cm. lead. He found that the absorption coefficient of the rays after filtration through about 4 cm. lead tended to a limiting value—the values found being $\mu = ·126$ in Al, $\mu = ·533$ in Pb. These values correspond to values for (μ_e/σ_0) of ·241 and ·295 respectively. The value ·241, which may be taken as equal

* K. W. F. Kohlrausch, *Phys. Zeits.* xxviii. p. 1 (1927).

to (σ/σ_0), is in good agreement with the value for the hardest components given by the Klein-Nishina formula (·286, ·250, and ·216). There can thus be little doubt that the Klein-Nishina formula is experimentally justified in the range of wave-lengths considered, and that the anomalous results with filters are due to secondary effects.

Discussion.

The main conclusion to be drawn from this investigation is that if the variation of the electron scattering coefficient with wave-length is that given by the Klein-Nishina formula, the results of the experiments from which the intensity distribution is estimated are consistent with those of the absorption experiments. For the unfiltered rays of RaB and C, the absorption coefficient estimated using the unmodified Dirac formula is about 25 per cent. lower than that observed; using the Klein-Nishina formula, there is agreement to within 2 per cent. This result is obtained when what seems to be a reasonable estimate of the efficiency of the ionization chamber is made.

It has, of course, long been realized that the results of absorption measurements with heterogeneous short wave-length radiation depend considerably on the ionization chamber used. The calculations which have been made indicate, by the consideration of limiting cases, the range of indefiniteness. In absorption experiments of this kind, a careful study of the characteristics of the ionization chamber is necessary. If the intensity distribution is known it should be possible to make a precise test of any absorption formula by choosing the ionization chamber suitably. The usual practice has been to use an ionization chamber which absorbs the radiations almost completely. This would be an ideal arrangement if the ionization current were strictly proportional to the absorption. This, however, is generally not the case. It would seem, therefore, better to use an ionization chamber in which the ionization current is closely proportional to the absorption, say a gas-filled chamber. Significant results would then be obtained if the fractional absorption were small. Then, if I_r is the initial intensity of the rth radiation, μ_r and μ_r' the absorption coefficients of the absorber and of the substance in the ionization chamber, the mean measured absorption coefficient would be given by

$$\bar{\mu} = \Sigma I_r \mu_r \mu_r' / \Sigma I_r \mu_r'.$$

An obvious elaboration of this method would be to make

measurements with two ionization chambers of different lengths. Corrections could then be made for the effects of the walls, which have recently been investigated, with electroscopes, by Chalmers *.

One of the most interesting applications of the absorption formulæ is to the determination of the wave-lengths of cosmic-rays. By analysing his depth-ionization curve, Millikan † finds that it can be accounted for by the presence of three approximately homogeneous groups of rays with absorption coefficients in water of ·35, ·08, and 0·4 metre^{-1}, corresponding to wave-lengths, with the Dirac formula, of about ·5, ·11, and $\cdot 06 \times 10^{-11}$ cm. The absorption per electron is related to the mass absorption by the formula

$$\sigma = \frac{\mu}{\rho} \times \frac{A}{NZ}$$

(μ is the absorption coefficient in cm.$^{-1}$, A and Z are the atomic or molecular weight and number, $N = 6{\cdot}06 \times 10^{-23}$).

For water ($\rho = 1$, $A = 18$, $Z = 10$) in which the photo-electric absorption is negligible, this gives

$$(\sigma/\sigma_0) = \frac{1}{\sigma_0} \frac{18}{10N} \mu = 4{\cdot}48\, \mu.$$

The calculated wave-lengths, using the two formulæ, are given in the following table :—

Calculated Wave-lengths of Cosmic Rays.

μ_{H_2O}. Metre^{-1}.	$\frac{\sigma}{\sigma_0}$.	$\lambda \times 10^{11}$ cm.	
		Dirac.	Klein-Nishina.
·35	·0156	·535	·161
·08	·00358	·117	·029
·04	·00179	·059	·013

These values may be compared with those corresponding to the upbuilding of atoms from protons and electrons, as suggested by Millikan, and the "annihilation" wave-length, corresponding to the conversion of the intrinsic energy of a proton into radiational energy.

* J. A. Chalmers, Phil. Mag. vi. p. 745 (1928).

† R. A. Millikan and G. Cameron, Phys. Rev. xxxi. p. 163 (1928); xxxi. p. 921 (1928); xxxii. p. 533 (1928).

Calculated Wave-lengths for Different Processes.

		$\lambda \times 10^{11}$ cm.
Upbuilding	He	·46
	N	·133
	O	·107
	Si	·057
Annihilation		·013

Using the Dirac formula, the smaller absorption coefficients do correspond to the upbuilding of nitrogen or oxygen (or both) and of silicon, but the agreement in the case of helium can hardly be regarded as satisfactory. There are strong reasons, which have been considered elsewhere *, for regarding Millikan's explanation of the origin of cosmic rays as highly improbable. Now that the Klein-Nishina formula has been shown to be consistent with the γ-ray results, while the Dirac formula is unsatisfactory, there is definite justification for using the modified formula for the cosmic rays. The revised wave-lengths could, of course, still be accounted for by the upbuilding of some atoms, but these would no longer be the most abundant ones; and the fact that the atoms required were abundant was considered to be a strong point in favour of the upbuilding explanation.

The absorption coefficient ·04 metre^{-1} does now correspond to the annihilation wave-length. Moreover, the scattered radiation is concentrated in a forward direction, and, as has been shown by Millikan, the mean wave-length is approximately twice that of the incident radiation. Thus the absorption coefficient ·08 ($\lambda = ·029$) may well be accounted for by the secondaries due to the annihilation wave-length radiation. The origin of the most strongly absorbed radiation, however, still remains obscure. Its relatively great intensity would appear to indicate that it is not to be explained by some secondary effect of the more penetrating radiation in any of the ways which have been considered.

There is very strong astronomical evidence for the view that mutual annihilation of electrons and protons must in some way occur. The objection that there is no indication of the corresponding radiation in the cosmic ray depth ionization curves now seems to be removed.

* E. C. Stoner, Proc. Leeds Phil. Soc. i. p. 349 (1929).

Summary.

A revised estimate of the intensities of the γ-rays of RaB and C has been made using the results of Ellis on the β-rays and on the γ-ray heating effect. If these results are correct, it is shown that the number of impulses counted by Kovarik is greater than the number of γ-ray quanta emerging from the disintegrating atoms.

The absorption coefficient which would be deduced with an experimental arrangement such as that of Ahmad is then calculated, using the Dirac and Klein-Nishina formulæ. The values obtained are in close agreement with the Klein-Nishina formula. The unmodified Dirac formula gives values about 25 per cent. too low.

The effect of filters is considered. Some of Ahmad's results appear anomalous, probably on account of secondary scattering effects. Kohlrausch's results with thick filters are consistent with the modified formula.

Suitable experimental arrangements for more precise tests of the formulæ are briefly discussed.

With the Klein-Nishina formula the most penetrating cosmic radiation observed by Millikan corresponds to the electron-proton annihilation wave-length.

Physics Department,
The University, Leeds.
January 1929.

XCIX. *The Raman Effect by Helium Excitation.* *By* R. W. Wood *.

[Plate XXI.]

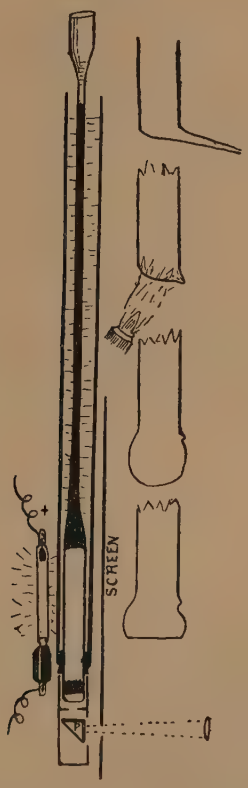
THE improved method of irradiating fluids by the light of the mercury arc, for the excitation of the Raman lines of modified wave-length, which I described in this Journal for Oct. 1928, has been still further improved, and though I have now abandoned the mercury arc for the helium lamp, which yields spectra excited by a pure monochromatic radiation, I think that a brief description of the new modification may prove helpful to workers in the field who lack facilities for the excitation by helium.

The disadvantage of the water-cooled tube which I described in the earlier paper was the necessity of using

* Communicated by the Author.

a large volume of an absorbing medium in a pail for supplying the cooling system in cases in which it was desired to suppress one or the other of the mercury lines. This was especially troublesome in the case of a solution of cobalt sulphocyanate, which I found much more effective in suppressing the 4358 group than a solution of fluorescein. The solution has to be very concentrated, however, and

Fig. 1.



I accordingly designed the cooling system shown in fig. 1, which accomplishes the desired result with a few hundred centimetres of fluid. The outer tube, preferably of thin pyrex glass, is 50 cm. long and has a diameter of 5 cm. The inner tube, with a diameter of 3·5 cm., is drawn down as shown in the figure, the portion indicated being painted with black "Duco" auto-enamel (a celluloid paint). The bottom of the tube is flattened, avoiding a lenticular button in the

centre, and the outer surface ground flat and polished. A flattened bulb, if properly made, acts quite as well, but is easily broken. The bulb should be blown in the stages shown in fig. 1, to secure an optically flat bottom. It should be very thin, and in flattening the bottom a vertical flame must be used, such as a Bunsen flame turned down very low, the tube being held in the vertical position. A round bulb cannot be used, as it acts as a short-focus lens when the tube is filled with liquid. The inner tube passes through a rubber gasket made from a stopper by cutting the ring out with a penknife while the stopper is spun with a lathe (see Phil. Mag. for Oct.). It is filled with the fluid to be observed to the upper end of the narrow portion, the widened top taking care of expansion. A cylinder of thin polished sheet aluminium is slipped around the lower part of the tube, embracing about two-thirds of its circumference, to serve as a reflector, and the outer tube then put in position, pressing the rubber gasket well into place, and securing it with thin copper wire. The space between the tubes is then filled with water or an absorbing solution, and the vertical quartz mercury arc mounted close to the wall, opposite the window in the aluminium reflector.

The cooling is effected by convection and radiation. With an apparatus of the dimensions given the temperature will come to rest at about 70° if the lamp is placed very close to the outer wall. In the case of liquids with boiling-points below 80° the lamp can be moved away a centimetre or two. Great care must be used with liquids having very low boiling-points, such as ether. It is well to keep a thermometer in the water, and move the lamp off as may be necessary. It is very important to screen the spectroscope from all rays except those issuing from the bottom of the tube, as by the method shown in fig. 1, in which the reflecting prism is contained in a black tube with suitable apertures and diaphragms. With an apparatus of this description one can photograph the stronger Raman lines with a small constant deviation spectroscope in two or three minutes. It can be operated without attention for hours or even over night, when using high dispersion. But at best the mercury arc is a very unsatisfactory source, owing to the impossibility of isolating a strictly monochromatic radiation from it.

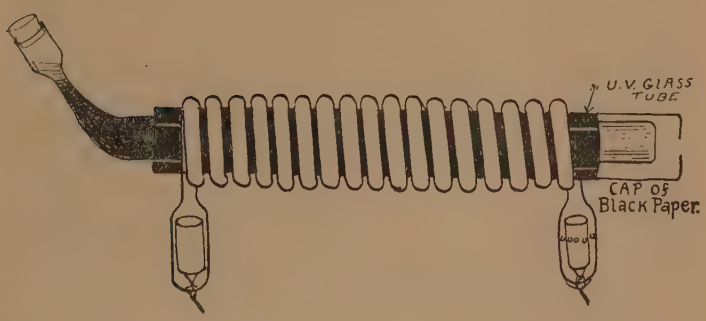
The close group of three lines at 4340–4358 yields a complicated spectrum, and the lines excited by 4046–4077 cannot be separated until all wave-lengths are measured, converted into frequencies, and the frequency differences compared.

It occurred to me that if a pure monochromatic excitation could be devised one might avoid all wave-length measurements and computations, for it would be necessary only to prepare a scale properly graduated to represent the infra-red wave-lengths associated with the Raman lines, and then enlarge the spectrogram to a suitable degree to fit the scale, and place the two in register. The infra-red wave-lengths could then at once be read off from the scale at each Raman line.

This cannot be done with the spectra made with the mercury arc for the reasons just given.

After considering all possible sources, I finally chose the helium vacuum tube as the most suitable, for the 3888·6 line is about 80 times as intense as any line in its immediate

Fig. 2.



vicinity when filtered by nickel oxide glass and all visible radiations are cut off. In preparing large blown cylinders of this glass during the war, for making ultra-violet "running lights" for ships in convoy, I had a few of them drawn out into long tubes, thinking that possibly Cooper-Hewitt lamps could be made of them. The tubes have been lying about my laboratory ever since, waiting for possible service. They proved to be exactly what I wanted. The tube containing the fluid under examination is slipped into the tube of nickel oxide glass and surrounded by a spiral tube provided with electrode bulbs and filled with helium at 8 mm., and excited by a 20,000-volt transformer.

The spiral discharge tube is cooled by an electric fan placed close to it, and I have had no difficulty in working with fluids boiling at 40°, the tube running over night without attention.

The ultra-violet glass transmits the light of the 3888 line at almost its full intensity, and to a much less degree the lines 3965 and 4025, but these are so feeble that I have never found a Raman line that could be attributed to them. The only disadvantage of their presence is that they may occasionally mask a Raman line that happens to coincide with them. Another advantage is that the entire Raman spectrum falls in a spectrum range over which the photographic plate shows nearly uniform sensitivity. With mercury 4358 excitation the lines corresponding to 3 μ absorption fall at about wave-length 5000, the region of minimum sensibility. In the case of the benzene, toluene, xylene, and similar compounds these lines are by far the strongest lines of the whole spectrum, while Raman listed the intensity as 1 on a scale of 10 for excitation by Hg 4358, which is precisely what one gets, even with a so-called orthochromatic plate. The presence of the other two helium lines on the plate is an advantage in one way, in that it aids one in fitting the photograph to the scale.

The 3888 line is so broadened by over-exposure that the setting must be done for this line by the edge of the spectrum corresponding to the end of the slit, where the broadened line comes to a blunt point.

The helium tube (of 10 mm. diameter) has a total length of 3 metres, but is wound into a spiral 6·5 cm. in diameter and 25 cm. in length. It was constructed by the Claude Neon Light Co. of Baltimore, and has cylindrical copper electrodes, which were very thoroughly outgassed before filling. After some two hundred hours of operation the tube has "gone-hard," and refuses to conduct. I am not at all sure of what has become of the 8 mm. of helium which it contained. The commercial tubes apparently do not give this trouble, but they are made of a yellow glass which would be quite unsuitable for 3880 transmission.

Spectra obtained with this apparatus of the lower alcohols and a number of benzene substitution compounds, including the three isomers of xylene and methyl cyclo-hexane, are reproduced as negatives on Pl. XXI.

The μ-scale is at the top, the graduations of which run all the way down the sheet, so that the infra-red absorption line corresponding to any Raman line can be read off at once. A scale of wave-lengths is added at the bottom.

The μ-scale was prepared in the following way. A photograph of the iron and helium spectra superposed was made with the prism spectrograph used for making the Raman

spectrograms (a small ancient model of Hilger's constant deviation fitted with a home-made plate-holder).

This was enlarged five-fold on a lantern-slide plate, which was in turn enlarged five-fold on a strip of bromide paper. The spectrum thus obtained from helium 3888 (the exciting-line used) to helium 4471 (the end of the Raman spectrum) measured 35 cm. in length, and the Raman spectra were enlarged to the same scale in the same way. Plate XXI. has been reduced about one-half from the original enlargements.

A scale of wave-lengths was prepared for the iron spectrum, and the wave-lengths were then calculated (from Kayser's table of frequencies), which corresponded to $3\,\mu$, $3{\cdot}1\,\mu$, $3{\cdot}2\,\mu$, etc., up to $100\,\mu$, by which we mean that the frequencies corresponding to these wave-lengths, when subtracted from the frequency of the helium 3888·6 line, give the frequencies corresponding to the divisions required for the μ-scale.

Tenths were calculated only up to $8\,\mu$, and above this as shown by the scale on the plate.

The values thus obtained were carefully marked on the wave-length scale, these marks giving the graduations of the μ-scale.

Having once prepared our scale we can determine immediately the wave-lengths of the infra-red absorption bands corresponding to the Raman lines by simply fitting the enlarged photograph to the scale. The enlargements should all be made on the same type of paper, and dried in the same way to avoid unequal shrinkage.

The values read off on the plate show slight errors, as it is difficult to mount a number of dry prints and not have some small expansions and contractions. For quantitative work I should be disposed to make a more accurate one than the one reproduced, which was a first attempt, and made in a hurry.

The advantage of the new method of excitation, and this short cut to the μ-values, will be obvious to anyone who has spent a whole day or more in measuring up a single Raman spectrum, computing the wave-lengths, looking up the frequencies, making the subtractions, and then searching out the lines which have a common excitation.

An alternative method, which would give results of greater accuracy and involve not much more time, would be to prepare a scale on which readings of the comparator were plotted against the μ-values, the scales being in coincidence. One would then merely mount the spectrogram in the comparator (set to zero say), and bring the helium exciting line on the cross-hairs. As each Raman line comes on the

cross-hair we take the reading and find the μ-value which corresponds to it on the double scale.

The original spectrograms from which Pl. XXI. was made were extremely sharp, but the total length of the spectrum was only 10 mm. I was unable to use my Bausch and Lomb spectrograph in the case of the helium excitation on account of the strong absorption of its prism for wave-lengths below 4050. The prism in the smaller Hilger instrument showed good transparency to below the exciting helium line.

I am having a new prism made for the B. and L. instrument, as a 25-fold enlargement puts too much of a strain on the enlarging apparatus for the finest detail. This was especially noticeable in the complicated groups of lines which correspond to the $3{\cdot}4\,\mu$ region. These groups I enlarged over again, first with a low-power microscope and then with the enlarging camera. They have been pasted over the poorly-defined images on the plate in the case of the benzene and related compounds. If this plate is compared with the one illustrating my paper in the Oct. 1928 number of this Journal, the enormous advantage of the helium excitation is at once apparent. We see immediately that the strong triple line of ethyl alcohol was excited by Hg 4046, while the line to the right of it was excited by 4358 corresponding to the line at $6{\cdot}8\,\mu$ by helium excitation. The line to the left of the triple line I have not yet reconciled with the helium photograph, for it does not appear in the methyl alcohol spectrogram. This matter will be further investigated.

The ease with which mistakes are made in the case of excitation by the mercury arc is illustrated by an example taken from Pringsheim's paper on the Raman effect (*Zeit. f. Physik*, l. p. 742).

In the first column of his table he gives the Raman line 4659 of benzene as excited by 4359, and also by 4078. In my earlier paper this line was referred to 4078 excitation, as it did not appear on plates made by mercury arc light from which the group 4046–4077 had been removed by a filter of potassium chromate. Pringsheim evidently assumed that it was excited also by 4358, as in this case it would be identified with the absorption band at $6{\cdot}75\,\mu$ found by Coblentz, which is the heaviest absorption band of benzene. The helium excitation confirms my earlier assignment of the line, for there is not the slightest trace of a line at $6{\cdot}75\,\mu$, showing that the strongest absorption band of benzene is not represented at all in the Raman spectrum.

The spectrum of benzene was photographed with the B. and L. spectrograph, with a rather long exposure to

ascertain the nature of the companion lines which border the 4407 line (3·3 μ). As I showed in a short note published in this Journal for Dec. 1928, this line is in reality double—a strong component about 1 Å.U. in width, bordered on the short wave-length side with a fainter broad companion. The photograph was made with a lens of 3-metre focus combined with a large plane grating of 6 in. diameter.

These companions were found to have the same structure as the very intense double line which they accompanied. A microphotometer curve was made for me on the Moll instrument at the Naval Research Laboratory, and is reproduced on Pl. XXI. I have put black dots under the companions. The faint line to the left is a very strong helium line, 4471, which probably reached the slit from the walls of the room. The dual nature of the main line was mostly obscured by over exposure, but it is very clear in the companions, which resemble two first- and one third-order "ghosts" of the main line (to use grating nomenclature). The photograph was made with a prism, however. It seems probable that these companions are related in some way to main lines. They appear unresolved on the benzene spectrum on the plate. To get them by combination we should have to have an absorption band at about 95 μ, and no Raman line appears at this point.

After working a month with helium excitation I should never think of returning again to the mercury arc. The question which the reader will ask is, of course, "How about getting tubes of nickel glass?" The only answer that I can give is that I am trying at the present time to induce some one or more of the glass mannfacturing companies to prepare tubing of this glass.

The glass which I made during the war seems to be rather superior to that which is on the market in America, having a sharper cut-off. I am now setting up an apparatus in which the illumination is to be by one of the new hot-cathode helium lamps (operating on 220 volts) developed in the research laboratory of the General Electric Co., and I am under great obligation to Drs. Whitney and Dushman, who furnished me with one of these lamps. The time of exposure will probably be much less than that required with the helium spiral, with which I give from five to fifteen hours.

The object of the present paper is to acquaint those who are working on the Raman effect with the new technique which I have employed, as an enormous amount of time is lost in working with the mercury arc. A discussion of lines in their relation to chemical constitution will be deferred to

a subsequent paper. A photograph such as the one reproduced will be a great help, as one can see at a glance the changes resulting from altering the structure of the molecule.

Prof. E. C. Kemble and Dr. E. L. Hill, of Harvard University, have worked out the quantum mechanical theory of the effect for HCl accounting for the sharpness of the single line, and the lines identified with alternate lines of the pure rotation band in the remote infra-red. Their paper will appear shortly in the Proc. Nat. Acad.

C. *The Effect of Ultra-Violet and X-Rays on the Steady Current Characteristics of Crystal Detectors. By* W. Jackson, *M.Sc., Lecturer in Electrical Engineering, Technical College, Bradford* *.

Introduction.

MANY theories have been put forward to explain the action of the crystal detector, but as yet no one of them has been accepted as completely satisfactory. As was the earlier coherer, this extremely sensitive detector, before being thoroughly understood, has been largely superseded by more reliable and stable methods of rectification. The gradual accumulation of data will, no doubt, in time lead to a theory capable of embracing and explaining the many phenomena which have been observed and recorded in published work on crystal detectors.

Dr. Eccles † has put forward a theory based on thermoelectric action at the light contact of the detector. It is supposed that the passage of current across the high-resistance junction of the two dissimilar metals or metallic compounds causes heat to be produced, and the local heating leads to the generation of a thermoelectric E.M.F. These thermal actions are very noticeable in contacts made of the badly conducting natural oxides or sulphides used in crystal detectors. This thermoelectric E.M.F. occurs during both the positive and negative half-cycles of the applied alternating voltage producing the current, during one of which it assists and during the other opposes, giving the phenomenon of asymmetric conduction. Complete rectification can only

* Communicated by the Author.

† Proc. Physical Soc. xxii. pp. 360 & 477 (1910); xxv. part iv. p. 273 (1913).

result when, during one half-cycle, the applied and thermo-electric E.M.F.'s accurately balance.

A. C. James * has attempted to substantiate the early electrolytic theories of crystal rectification. He suggests that the passage of a direct current through galena (the crystal under his investigation), the negative contact being a metallic point, is accompanied by the electrolytic formation of metallic threads across the contact; while, when the point is positive, a high resistance film is formed. He explains the unidirectional conductivity and rectification from a consideration of the crystal structure, and by the fact that in solid electrolytes the current is carried entirely by one set of ions, the other forming a fixed framework. In rectification the metal ions are supposed to oscillate to and fro through fixed channels in the high-resistance film, giving metallic and non-metallic contact alternately during the two half-cycles of the applied E.M.F. The reason given for the variation of the rectifying properties at different points on the crystal surface is that the metal ions can move without collision in some planes of the crystal, but not in others.

A more recent theory put forward by W. Ogawa † states that the rectification is brought about by the difference of electron emissions from the two electrodes forming the contact, and that thermoelectric and electrolytic effects do not enter into the question. He shows that rectification is possible by two electrodes of different electron emissions separated *in vacuo* in the cold state, and that the direction of the rectified current is the same as that in a contact detector composed of the same electrode materials. In effect the crystal is a cold vacuum-tube operating as a detector by the differences in electronic emissions of its electrodes.

L. S. Palmer ‡ suggests that this analogy with the thermionic valve is supported by the observed phenomena that improved rectifying properties are obtained when the tendency for electronic emission is increased. Most crystals exhibit increased rectifying efficiency when a small steady potential is applied across the contact of such polarity as to produce a current in the same direction as the rectified current. A similar effect has been noticed when the crystal contact is heated.

The result of adding a small quantity of impurity is to improve the rectification, and suggests that the impurity

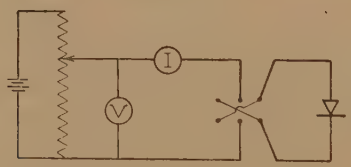
* Phil. Mag. xlix. p. 681 (1925).
† Phil Mag., July 1928, p. 175.
‡ Palmer, 'Wireless Principles and Practice,' p. 304.

increases the electronic emission from the crystal. That certain faces of the crystal appear to be better than others as regards rectification may be explained by this if the points of maximum rectification are found where thin layers of impurities, included in the crystal during the process of formation, exist. This seems likely since the purest crystals exhibiting normal crystalline form show no very sensitive spots, while those exhibiting variation in form from the normal usually have many *. These phenomena seem to indicate that the rectifying properties of a substance may be expected to be appreciable if the work necessary to remove an electron is small †.

Experimental.

The steady current characteristic of a crystal detector, that is, the curve connecting the current flowing through the crystal contact and the steady applied voltage, enables one to determine whether a given crystal will rectify efficiently

Fig. 1.



and what value of potential, steadily applied, will make the degree of rectification a maximum. The characteristic may be determined by means of the circuit of fig. 1, in which I is a microammeter and V a voltmeter of high resistance compared with that of the contact. The points on the characteristic for which the second differential is a maximum give the points for best rectification.

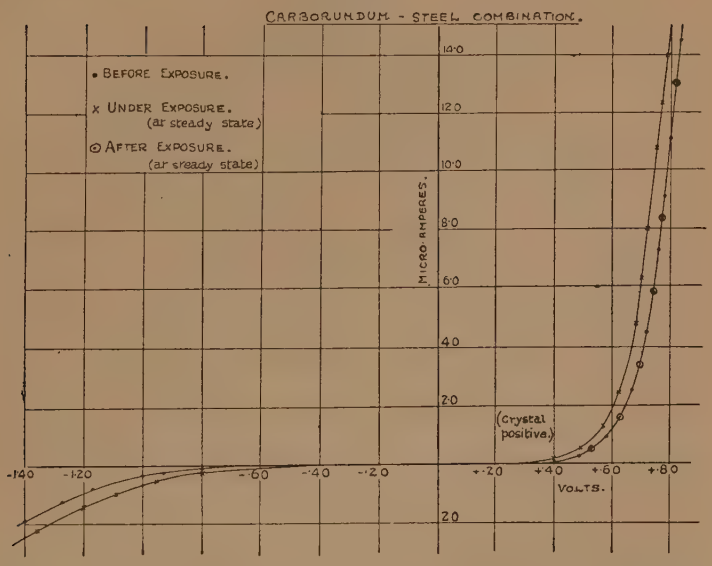
Effect of Ultra-violet Light.

The characteristic curve of the crystal under test was determined before exposure to the ultra-violet light. The source of light was a medical quartz mercury-vapour lamp, without filter, consuming 4 amperes from a 230 volt direct-current supply. The light-spectrum of this lamp covers a wave-length band from 0·43 to 0·23 millimicrons. The output of heat rays is stated to be very low. During

* H. Pélabon, *Comptes Rendus*, clxxii. p. 143 (Jan. 11, 1926).
† Palmer, ' Wireless Principles and Practice,' p. 303.

exposure the crystal was supported at a distance of one foot from the tube, the rays from which were allowed to play directly upon the crystal contact. A small steady potential was applied to the crystal and the change of current, flowing under the influence of this applied pressure, with time of exposure noted. When the current had reached a steady value, the characteristic curve was redetermined under exposure. Before extinguishing the mercury-vapour lamp, the applied voltage to the crystal was adjusted to the same value as that during exposure, and the change of current

Fig. 2.



observed after the rays had been cut off. A final characteristic curve was determined when the current again reached a steady value.

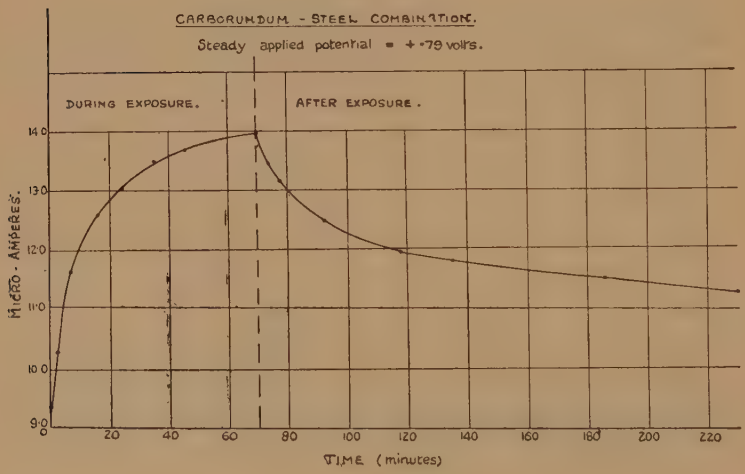
The curves of fig. 2 show the results obtained with a carborundum-steel combination. During exposure there occurred a rise in current, rapid at first, but more slowly as the steady state was approached. The nature of the current change is shown in fig. 3. This increase in conductivity of the crystal contact is seen from fig. 2 to be more pronounced for positive than for negative applied voltages. The steady state under the ultra-violet light was not reached until after an exposure of more than an hour. After extinguishing the

arc the fall in current which resulted was very slow, but after a period of several hours the crystal had reached its original state and provided the same characteristic as before exposure.

Similar tests were performed on hertzite, galena, and silicon crystals, using a silver wire as contact-point. Of those tested, the crystal on which the effect of the rays was most pronounced is known by the trade name "Stutzberg." The results with this crystal are given in figs. 4 and 5.

An examination of the characteristic curves of the several crystals tested, taken before and at the steady state during exposure, leads to the conclusion that along with the increased

Fig. 3.



conductivity of the crystal contact under the rays, there occurs a slight decrease in value of the maximum curvature of the characteristic, and with this a reduction in the rectifying properties at the point of best rectification.

Effect of X-Rays.

The same procedure as described above was adopted in examining the effect of exposure to X-rays. During exposure the crystal was supported at a distance of 4 inches below the X-ray tube. The quality of the rays used was 8 Benoist. There occurred an increase in current through the crystal with time of exposure, rapid at first and more slowly as the steady state was approached. As the

Fig. 4.

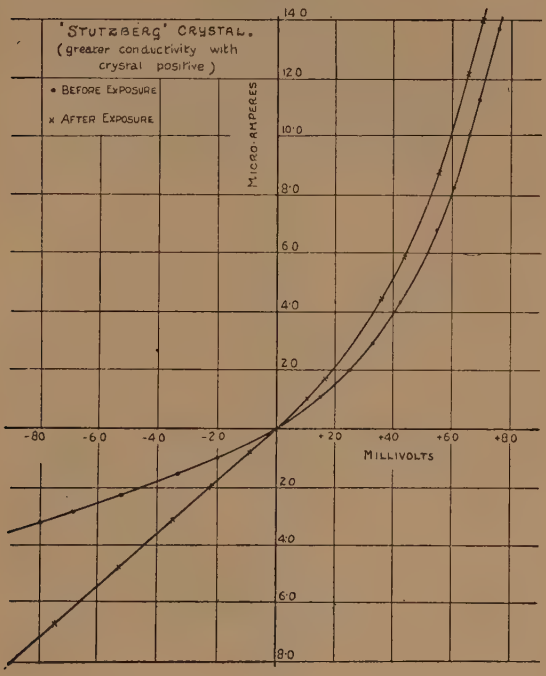
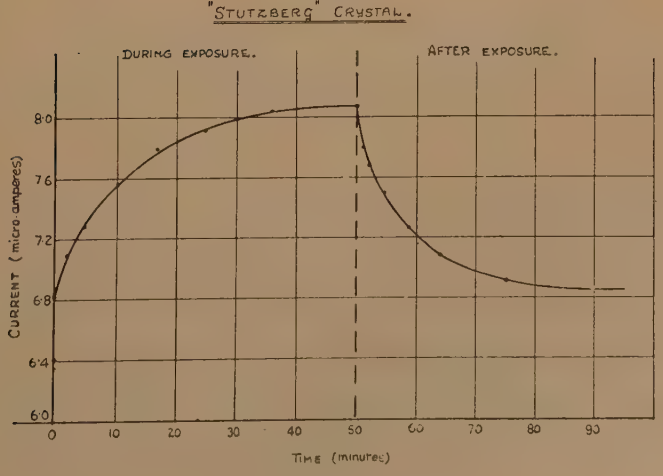

'STUTZBERG' CRYSTAL.
(greater conductivity with crystal positive)
• BEFORE EXPOSURE
x AFTER EXPOSURE
MICRO-AMPERES
14·0
12·0
10·0
8·0
6·0
4·0
2·0
-80
-60
-40
-20
+20
+40
+60
+80
MILLIVOLTS
2·0
4·0
6·0
8·0

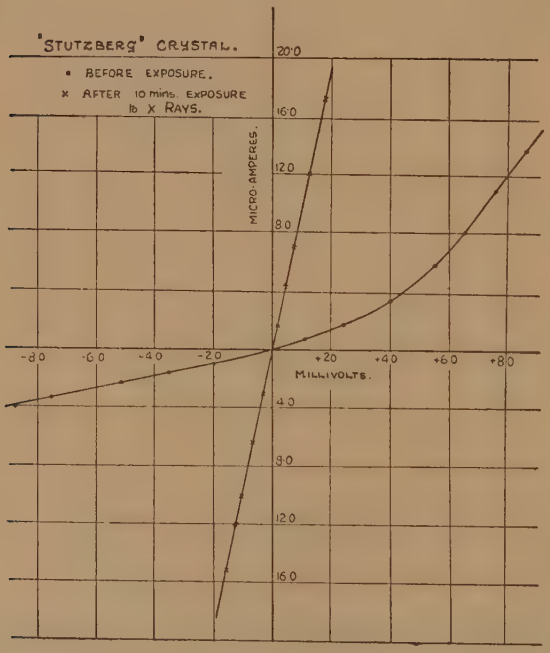
Fig. 5.


"STUTZBERG" CRYSTAL.
DURING EXPOSURE.
AFTER EXPOSURE.
CURRENT (micro-amperes)
8·0
7·6
7·2
6·8
6·4
6·0
0
10
20
30
40
50
60
70
80
90
TIME (minutes)

changes in current were not gradual but often took place in jerks, it was not possible satisfactorily to plot a curve showing the nature of the change with time.

In the case of the hertzite, galena, silicon, and "Stutzberg" crystals, the unidirectional and rectifying properties were completely destroyed, and even after several hours of rest there was no indication of a recovery of these properties. Fig. 6 shows the results on the "Stutzberg" crystal, those

Fig. 6.



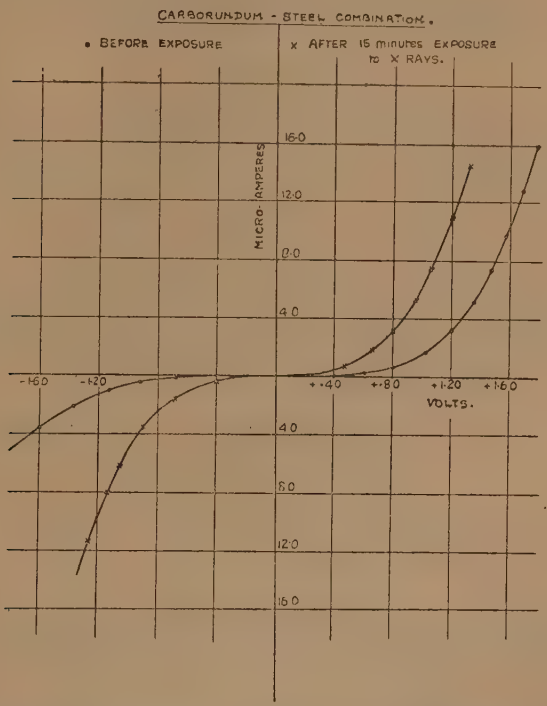
relating to the other crystals mentioned being essentially similar in nature.

With the carborundum-steel combination, the results on which are given in fig. 7, the loss of unidirectional property is noticeable although the rectifying property is retained for both positive and negative values of applied voltage.

It has not been possible to draw any definite conclusions from the results obtained during the short opportunity presented for carrying out the recorded work. Their statement may, however, prove of interest and suggest possibilities

for future investigation, which may help to substantiate one or other of the above summarized theories of crystal rectification.

Fig. 7.



The writer's thanks are due to Dr. Williams, School Medical Officer for Bradford, and to Mr. W. H. N. James, of the Technical College, for the facilities provided.

CI. *On the Effect of Constrictions in Kundt's Tube and Allied Problems.*—II. *Some Theoretical Considerations.* *By* Eric J. Irons, *B.Sc.*, *East London College*, *E.* 1 *.

1. Introduction.

In a previous paper [1] the results of experiments to determine the effect of introducing diaphragm constrictions on the distribution of nodes and antinodes in a Kundt's sound-tube apparatus were described, and some measurements of

* Communicated by the Author.

the end corrections of a partially-stopped tube were recorded. In the present communication these results are examined by the principles of "acoustical impedance" introduced by Webster[2] and, in addition, formulæ giving the proper tones of various simple forms of resonator are derived.

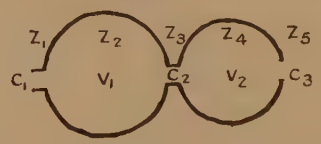
2. Theoretical.

According to Stewart[3] the impedances of an orifice, reservoir, pipe with a closed end, and pipe with an open end may be taken as

$$\frac{i\rho\omega}{c}, \quad \frac{-i\rho a^2}{\omega V}, \quad \frac{-i\rho a}{S}\cot\frac{\omega L}{a}, \quad \frac{i\rho a}{S}\tan\frac{\omega L}{a} \quad . \quad (1)$$

respectively *, where $i = \sqrt{-1}$, ρ = density of medium, a = velocity of sound, $\omega = 2\pi$ (frequency), V = volume of reservoir, c = conductance of orifice, and S and L are area of cross-section and length of pipe respectively.

Fig. 1.



Terms involving "radiation resistance" and friction are neglected as small compared with the terms retained.

The natural tones of a number of common forms of resonator are easily calculated by the application of the above formulæ, and, as they may be of service as mnemonics, formulæ for some ten forms are tabulated below. This paper is primarily concerned with two of these forms (numbers 5 and 6).

(1) *Rayleigh Double Resonator.* (Fig. 1.)

The resonator consists of two reservoirs of volumes V_1 and V_2, communicating with each other and with the external air by passages having conductances c_2, c_1, and c_3 respectively. Let Z_1, Z_2, Z_3, ... (fig. 1) represent the impedances of the different elements of the resonator. The medium in V_1 may, when displaced, flow through either of the passages of con-

* It may be noted that if the length L of the pipe be so small that $\tan \omega L/a$ may be replaced by $\omega L/a$, then the expression for the impedance of a closed pipe reduces to that of a reservoir, while the value for an open pipe becomes identical with that of an orifice.

ductance c_1 or c_2, which must therefore be considered in parallel. Suppose the impedance of Z_3, Z_4, and Z_5 considered as one unit be represented by P, then the combined impedance of Z_1 and P in parallel must be considered in series with Z_2, and for resonance the resultant must be equated to zero. Thus

$$\frac{PZ_1}{P+Z_1}+Z_2=0.$$

Similarly, considering the motion of the fluid in V_2 and supposing the impedance of Z_1, Z_2, and Z_3 considered as one unit to be P′, we have

$$\frac{P'Z_5}{P'+Z_5}+Z_4=0.$$

Finally, P and P′ (*both* of which include Z_3) may be considered in series ; so that for resonance

$$P+P'-Z_3=0.$$

Eliminating P and P′ from these equations gives

$$\frac{Z_1Z_2}{Z_1+Z_2}+\frac{Z_4Z_5}{Z_4+Z_5}+Z_3=0,$$

and substituting the appropriate values from equation (1), we have

$$\omega^4-a^2\omega^2\left\{\frac{c_1+c_2}{V_1}+\frac{c_2+c_3}{V_2}\right\}+\frac{a^4}{V_1V_2}\left\{c_1c_3+c_2(c_1+c_3)\right\}=0, \quad . \quad . \quad . \quad . \quad (2)$$

which is in agreement with Rayleigh's [4] result obtained by the method of Lagrange *.

(2) *Helmholtz Double Resonator.* (Fig. 2.)

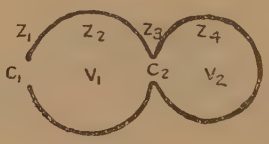
The formula for this type of resonator has been obtained on impedance principles by Richardson [5] and on different grounds by Paris [6]. Following Rayleigh, the formula may be obtained directly from equation (2) by putting $c_3=0$, when

$$\omega^4-a^2\omega^2\left\{\frac{c_1+c_2}{V_1}+\frac{c_2}{V_2}\right\}+\frac{a^4c_1c_2}{V_1V_2}=0, \quad . \quad (3)$$

* Rayleigh contemplates the frequency of the natural tones to be given, in his notation, by $n^2=-p^2/4\pi^2$, which accounts for the positive coefficient of p^2 in his equation.

or, following Richardson, by adding Z_3 and Z_4 in series, taking the resultant of these in parallel with Z_1 and equating the series sum of this quantity and Z_2 to zero.

Fig. 2.



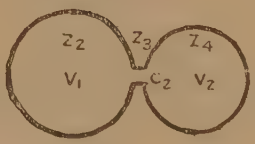
(3) "*Dumb-bell*" *Resonator.* (Fig. 3.)

From first principles, $Z_2+Z_3+Z_4=0$ for resonance, and, substituting the appropriate values from equation (1), we have

$$\omega^2-a^2c_2\left(\frac{1}{V_1}+\frac{1}{V_2}\right)=0, \quad . \quad . \quad . \quad . \quad (4)$$

which agrees with the result obtained from equation (3) by putting $c_1=0$.

Fig. 3.



(4) *Reservoir with two (or more) openings.*

In equation (2) put $V_2=\infty$ and

$$\omega^2-a_2\left(\frac{c_1+c_2}{V_1}\right)=0, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or, from first principles, add the impedances of the openings in parallel, and, to the result, add the impedance of the reservoir and equate to zero for resonance. (See [4].)

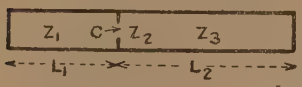
(5) *Constrictions in Kundt's Tube.* (Fig. 4.)

If the reservoirs of (3) be replaced by closed pipes, and the passage of conductance c_2 by a diaphragm pierced by a circular hole, we have, for resonance, substituting the impedance of a closed pipe for that of a reservoir, or, alter-

natively, substituting the appropriate values in the equation $Z_1+Z_2+Z_3=0$,

$$\frac{\omega}{c}=\frac{a}{S}\left(\cot\frac{\omega L_1}{a}+\cot\frac{\omega L_2}{a}\right). \quad . \quad . \quad . \quad . \quad (6)$$

Fig. 4.



(6) *Partially-stopped Pipe, or Helmholtz Resonator of Cylindrical Form.*

If one of the pipes, say L_2, of (5) is removed, we are left with a partially-stopped pipe or Helmholtz resonator, for the natural frequencies of which

$$\frac{i\rho\omega}{c}-\frac{i\rho a}{S}\cot\frac{\omega L}{a}=0$$

or

$$\tan\frac{\omega L}{a}=\frac{ac}{\omega S}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

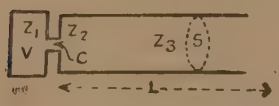
an equation deduced on these lines by Richardson (*loc. cit.*) and previously given by Rayleigh (*loc. cit.*).

(7) *Boys Resonator.* (Fig. 5.)

This consists of a pipe open at one end and having an orifice leading to a resonator at the other end. Let the quantities involved be as shown in fig. 5, L being the length of the pipe including the end correction, so that for resonance $Z_1+Z_2+Z_3=0$, or, in terms of equation (1),

$$\frac{i\rho\omega}{c}-\frac{i\rho a^2}{\omega V}+\frac{i\rho a}{S}\tan\frac{\omega L}{a}=0,$$

Fig. 5.



which, writing the frequency of the resonator with orifice when separated from the rest of the system as $n_1\left(=\frac{a}{2\pi}\sqrt{\frac{c}{V}}\right)$,

gives

$$\tan\frac{\omega L}{a} = -\frac{2\pi S}{ac}n_1\left(\frac{n}{n_1}-\frac{n_1}{n}\right), \quad . \quad . \quad . \quad (8)$$

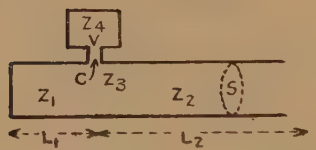
which is the result obtained by Paris [6].

(8) *Stopped Pipe with Helmholtz Resonator on the side.* (Fig. 6.)

The medium in the pipe of impedance Z_2 may, when displaced, move either into the pipe of impedance Z_1 or through the orifice into the resonator. It follows that Z_1 and (Z_3+Z_4) must be added in parallel, the result increased by Z_2, and the whole be equated to zero for resonance. Thus

$$Z_2+\frac{Z_1(Z_3+Z_4)}{Z_1+Z_3+Z_4}=0,$$

Fig. 6.



which, after some reduction, gives, on substituting the appropriate values from equation (1),

$$-\frac{2\pi S}{ac}.n_1\left(\frac{n}{n_1}-\frac{n_1}{n}\right)=\frac{1}{\cot\frac{\omega L_2}{a}-\tan\frac{\omega L_1}{a}}$$

$$=\frac{1}{\cot kl'-\tan k(L'-l')} \quad (9)$$

in the nomenclature of Paris (*loc. cit.*).

(9) "*Bottle-pipe*" *Resonator.*

Aldis [7] has given a formula for the natural tones of a resonator of the form of fig. 7 : it is readily obtained by adding the impedances of an open pipe and a closed pipe in series, when

$$-\frac{i\rho a}{S_2}\cot\frac{\omega L_2}{a}+\frac{i\rho a}{S_1}.\tan\frac{\omega L_1}{a}=0$$

or

$$\tan\frac{\omega L_1}{a}.\tan\frac{\omega L_2}{a}=\frac{S_1}{S_2}. \quad . \quad . \quad . \quad (10)$$

Paris [8] has pointed out that this formula embodies Rayleigh's formulæ for the natural tones of a Helmholtz resonator, a stopped pipe with restricted mouth, and a long tube connected with a reservoir of small volume.

Fig. 7.

(10) *Rohrflöte.*

Benton [9] has drawn attention to the Rohrflöte pipe, in which the "stopped" end is fitted with an open chimney. In this instance the impedances of two open pipes must be added in series, when

$$\tan\frac{\omega L_1}{a}\Big/\tan\frac{\omega L_2}{a} = -r^2/R_2 \quad . \quad . \quad . \quad (11)$$

(r and R being the radii of the lengths L_1 and L_2 of the chimney and pipe respectively), which is the result given by Benton.

3. Examination of previous Experimental Work in the light of the above Theory.

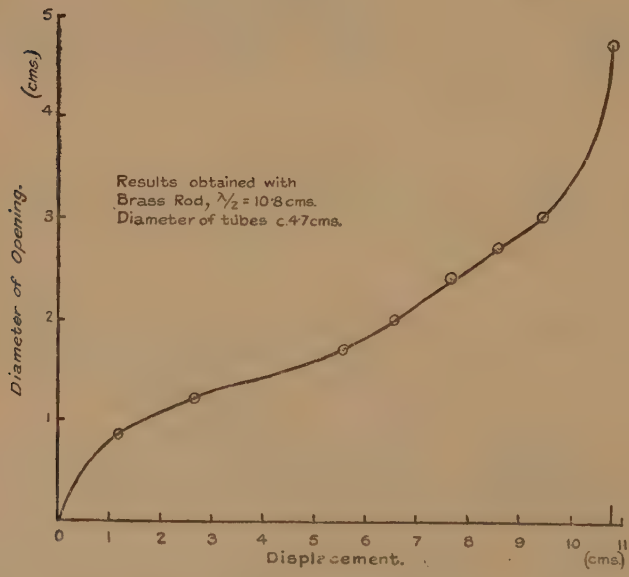
Part I. *Experiments with Constrictions.*

Full details of the experimental work are given in the paper cited [1]. It will suffice here to state that a diaphragm was placed between two glass tubes one of which was fitted with a movable stopper, while into the other the end of a rod, suitably clamped and fitted to serve as a source of sound, was allowed to protrude—the whole forming a "Kundt's tube with constriction."

Two types of experiment were carried out. In the first the mode of production of *good dust figures* was investigated. The results occurred in two groups, in both of which the antinodes in the two tubes were found to be symmetrically placed with respect to the constriction. In Group A no displacement of the antinodes was found, *i. e.*, the constriction appeared to form a node whatever the area of the opening in the constriction; while in Group B the antinodes were moved out from the constriction in both tubes to an extent shown in fig. 3 of the experimental paper.

Although the positions of the antinodes were measured and recorded it will be more convenient here to deal with the positions of the nodes, spaced midway between the antinodes in each tube, and to redefine the "Displacement" as the distance between the *nodes* nearest to the constriction in each tube. Thus, when the constriction is entirely closed (nodes coinciding with constriction in both tubes), the displacement will be zero; and when the constriction is "open" (and, according to results of Group B, an antinode may be considered as situated at it) the displacement will be a quarter wave-length in respect to each tube, and therefore

Fig. 8.



half a wave-length in all. The experimental results are shown in fig. 8, which is a graph of displacement against the diameter of opening in the constriction for a half wave-length of 10·8 cm.

In what follows it will be necessary to neglect energy losses due to reflexion and to friction so that the nodes may be considered as planes of no motion and, theoretically, may be replaced by solid walls.

Equation (6)—

$$\omega = \frac{ac}{S}\left(\cot\frac{\omega}{a}L_1 + \cot\frac{\omega}{a}L_2\right)$$

(where L_1 and L_2 represent the distances between the constriction and the nearest nodes in each tube)—may then be applied to the system. For results of Group B, $L_1 = L_2 =$ half of the displacement D, as defined above, whence

$$c = \frac{\omega S}{2a} \tan \frac{\omega}{a} \cdot \frac{D}{2}$$

$$= \frac{\pi S}{\lambda} \tan \frac{\pi}{\lambda/2} \cdot \frac{D}{2}, \quad \ldots \ldots \quad (12)$$

substituting for ω in terms of the wave-length λ, which was 21·6 cm.

By substituting the Group B data for this wave-length in equation (12), the following table of conductances has been prepared for the openings of the various constrictions placed in a tube of cross-sectional area of 17·3 sq. cm.

Diameter of orifice :

·84, 1·2, 1·7, 2·0, 2·4, 2·7, 3·0 cm.

Conductance :

·44, 1·0, 2·7, 3·6, 5·2, 7·6, 13·2 cm.

The second type of experiment was concerned with tracing, with any one constriction, *the positions of the anti-nodes (or nodes) corresponding to given positions of the stopper*, and the results obtained in a particular instance are indicated in fig. 4 of the experimental paper [1]. Under these conditions equation (6) will take the form :

$$\cot \pi \frac{L_1}{\lambda/2} + \cot \pi \frac{L_2}{\lambda/2} = \frac{2\pi S}{\lambda c} = K \text{ (a constant)}. \quad (13)$$

This equation has been tested for the instance quoted by assigning values to L_2 and, using the value of c determined by equation (12) *, calculating the corresponding values of L_1. Fig. 9 is a reproduction of fig. 4 of the experimental paper [1], and shows the agreement between experiment and theory.

In general it is convenient to discuss equation (13) graphically by means of the following construction (fig. 10).

On XY set off a length AB = K. Parallel to, and at unit distance from XY draw another line MN. At A set off

$$\widehat{BAC} = \frac{\pi L_1}{\lambda/2},$$

cutting MN in C. Join CB. From C draw a perpendicular to XY meeting it in D.

* This is tantamount to fixing one point on the L_1 curve.

Fig. 9.

⊙ Positions of Antinodes
↓ „ „ Nodes } Determined by experiment.
↑ Calculated positions of Nodes.
1 Indicates point an integral number of half wave-lengths from stop.
Symmetry corresponding to :—

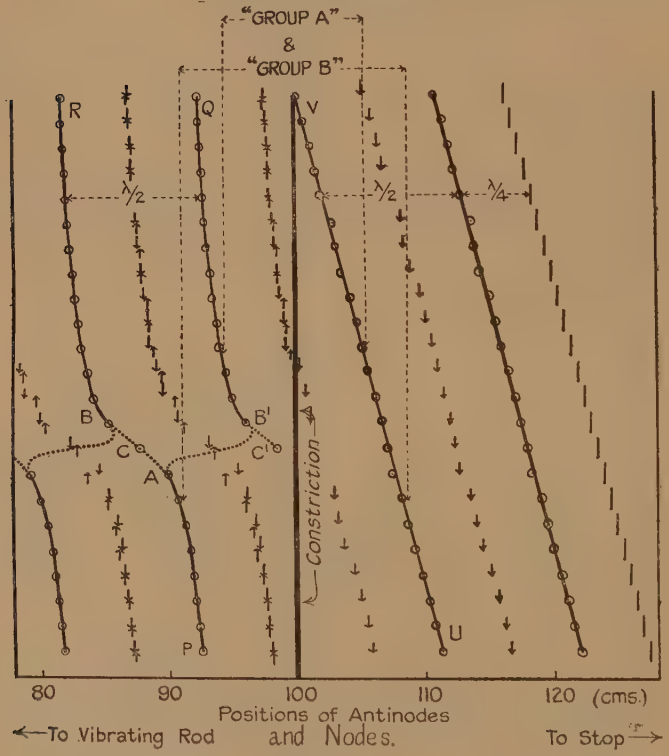
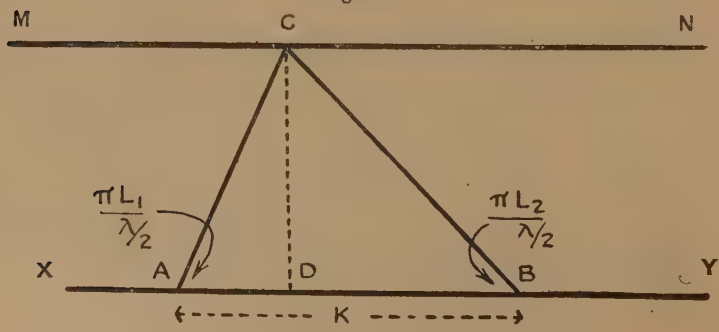


Fig. 10.



Then $$AD=\cot\frac{\pi L_1}{\lambda/2}, \quad AB=K,$$

so $$DB=\cot\frac{\pi L_2}{\lambda/2} \quad \text{and} \quad \widehat{CBD}=\frac{\pi L_2}{\lambda/2}.$$

Hence, if K be known, the value of L_2 corresponding to any value of L_1 (or *vice versâ*) may be obtained from the figure.

Three notes are appended which show the general agreement between the facts observed and recorded in the experimental paper [1] and deductions from the above construction based on theory:—

(*a*) If the opening in the constriction be large, *c* is large, K is correspondingly small, and $\widehat{ACB}$ is small so that

$$\frac{\pi L_1}{\lambda/2}+\frac{\pi L_2}{\lambda/2}=\pi-\widehat{ACB}=\pi \text{ (approx.)} \quad \text{and} \quad L_1+L_2=\lambda/2\ ;$$

i.e., the effect of the constriction is small and nodes (or antinodes) in both tubes are in step in spite of the presence of the constriction.

(*b*) If the opening in the constriction be small, *c* is small and K is correspondingly large. It follows that $\widehat{ACB}$ will usually be large and $\frac{\pi(L_1+L_2)}{\lambda/2}$ small; *i.e.*, L_1 and L_2 will both be small and the nodes will be near the constriction in both tubes.

(*c*) $L_1=L_2$ when

(i.) $\widehat{CAB}=\widehat{CBA}$ corresponding to Group B results,

and (ii.) when $\frac{\pi L_1}{\lambda/2}=\pi$, $\frac{\pi L_2}{\lambda/2}=0$, and *vice versâ*; *i.e.* $L_1=L_2=0$ or $\lambda/2$, or the nodes coincide with the constriction as in Group A results.

Part II. *Experiments with Caps.*

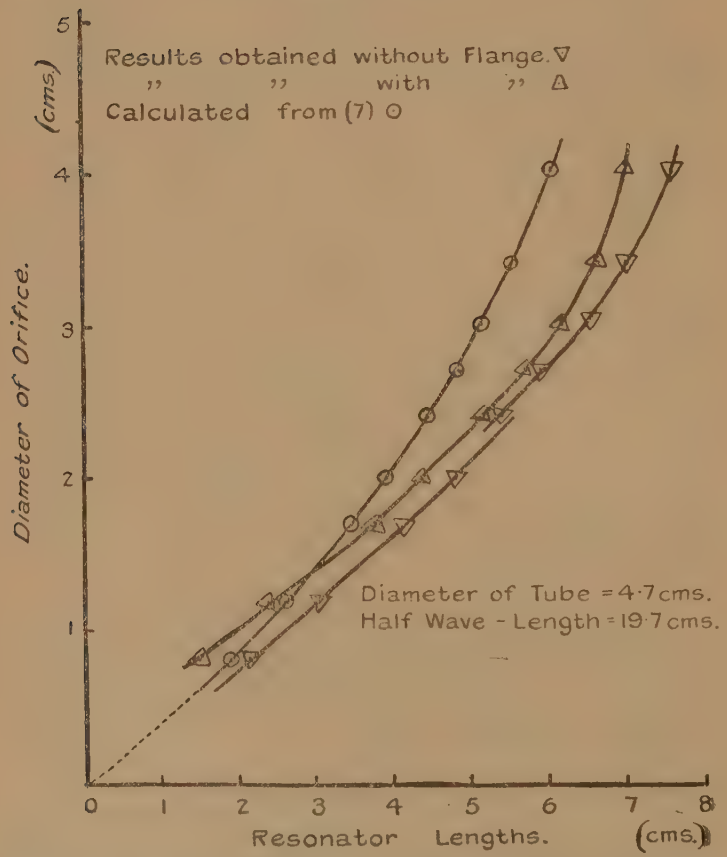
We pass finally to the consideration of equation (7) in the light of results obtained by placing caps, having orifices of various diameters, on the end of a single Kundt's tube. The discussion will be restricted to the results shown in fig. 7 of the experimental paper [1], as they correspond to the largest half wave-length (19·7 cm.) and are therefore most in accordance with the postulates of theory. For convenience these results have been replotted (fig. 11) with L (the distance of the nearest node from the cap or the "length"

of the resonator {$=\lambda/4-$end correction}) as abscissa, and the diameter of the orifice in the cap as ordinate.

As Richardson (*loc. cit.*) has pointed out, equation (7),

$$\tan\frac{\omega L}{a}=\frac{ac}{\omega S} \quad \text{or} \quad \tan\frac{\pi L}{\lambda/2}=\frac{\lambda}{2\pi}\cdot\frac{c}{S},$$

Fig. 11.

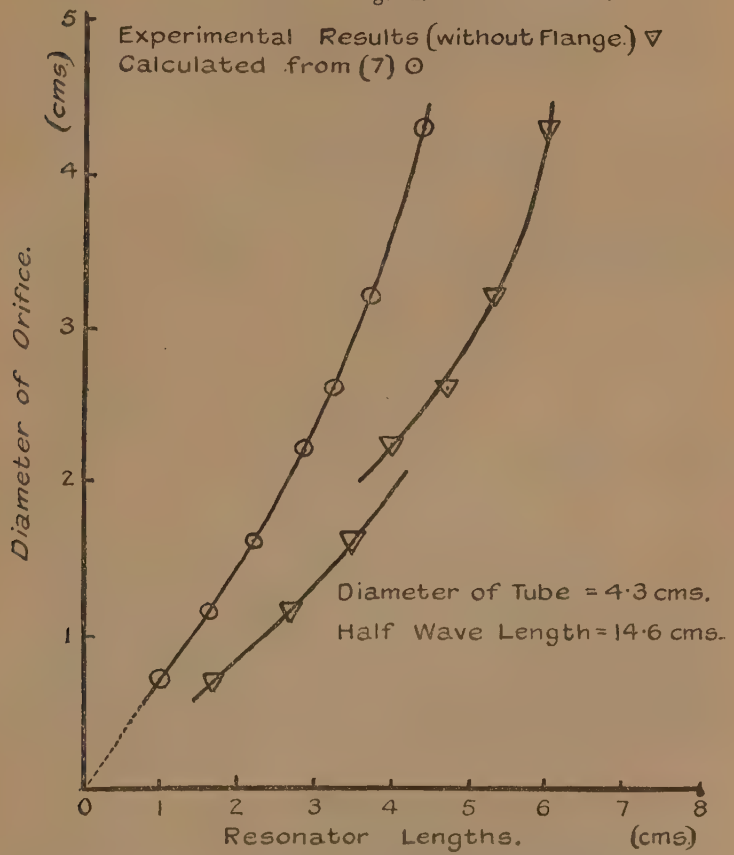


embraces both the "resonator" and the "pipe" formulæ. Assuming c, the conductance of the orifice, to be equal to the diameter of the orifice, the values of L calculated from equation (7) may be compared with those observed by reference to fig. 11 of this paper. Richardson's observed values (obtained by the Blaikley method), together with those calculated from equation (7) in the instance most similar as regards wave-length and diameter of tube to the one under

consideration, have been graphed on the same scale for comparison (fig. 12).

It will be seen that the discontinuity observed by the present author for an unflanged pipe occurs on Richardson's curve; it may also be observed in the other results he quotes.

Fig. 12.



Equation (7) furnishes a justification for two empirical les given in the former communication [1].

First, if c is small, then $\tan\frac{\omega L}{a}$ is small, and may be replaced by $\frac{\omega L}{a}$, so that

$$\omega = a\sqrt{\frac{c}{L.S}} = a\sqrt{\frac{2r}{L.S}},$$

where r is the radius of the opening in the cap. Hence, S and ω being constant, $(r/L)^{\frac{1}{2}}$ should be constant as previously explained [1].

Second, if in equation (7) we denote end correction by e and write for L, $(\lambda/4-e)$, then

$$\tan\frac{\pi L}{\lambda/2}=\tan\frac{\pi(\lambda/4-e)}{\lambda/2}=\cot\frac{\pi e}{\lambda/2}=\frac{\lambda\,.\,c}{2\pi\,.\,S}$$

or

$$c\tan\frac{\pi e}{\lambda/2}=\frac{2\pi S}{\lambda}.$$

Further, for flanged caps with openings between 1 and 2 cm. radius and a half wave-length of 19·7 cm., we have approximately $2{\cdot}5 < e < 5{\cdot}0$, *i. e.*, $\frac{\pi}{8}<\frac{\pi e}{\lambda/2}<\frac{\pi}{4}$ and, very roughly, we may replace the tangent over this range by 1·2 times the angle so that

$$c\,.\,1{\cdot}2\,.\,\frac{\pi e}{\lambda/2}=\frac{2\pi S}{\lambda}$$

or

$$c\,.\,e=\frac{S}{1{\cdot}2}=\frac{17{\cdot}1}{1{\cdot}2}=14{\cdot}3,$$

inserting the value of the cross-sectional area of the tube. Now, by experiment it was found that

$$r\,.\,e=5{\cdot}5 \quad \text{or} \quad (2r)\,.\,e=11{\cdot}0,$$

where r was the radius of the hole in the cap. Rayleigh (*loc. cit.*) has suggested that the conductance of an orifice is equal to its diameter, but, to reconcile theory with practice, the conductances of the orifices in question must be assumed to be somewhat greater than their diameters, and this might reasonably be expected, considering that the radius of the tube was only about 2·5 cm.

References.

(1) Irons, Phil. Mag. v. p. 580 (1928).
(2) Webster, Proc. Nat. Acad. Sci. v. p. 275 (1919).
(3) Stewart, Phys. Rev. xx. p. 528 (1922) *et sqq.*
(4) Rayleigh, Phil. Trans. clxi. p. 77 (1870), or Scient. Papers, i. p. 33 (1899).
(5) Richardson, Proc. Phys. Soc. xl. p. 206 (1928).
(6) Paris, Proc. Roy. Soc. A, ci. p. 391 (1922); Phil. Mag. xlviii. p. 769 (1924).
(7) Aldis, 'Nature,' cxiv. p. 309 (1924).
(8) Paris, *ibid.* p. 465 (1924).
(9) Benton, *ibid.* p. 573 (1924).

CII. *Coefficient of Cubical Expansion of Liquids and Critical Temperature.* *By* V. N. Thatte, *M.Sc.*(*Allahabad*) *.

In the Phil. Mag. for April 1912 Mr. Davies gives a relation between the coefficient of cubical expansion of a liquid and its critical temperature. The relation is based on Mathias's law of rectilinear diameters and Guldberg's calculation of the ratio of densities of a liquid at 0° C. and at the critical temperature.

Mr. Davies finds that the relation

$$C=\frac{1}{v}\left(\frac{dv}{dT}\right)_p=\frac{1}{2T_c-T}$$

is true for a number of liquids, where C is the coefficient of expansion of a liquid, T_c is the critical temperature on the absolute scale, and T is the absolute temperature at which the coefficient of expansion is measured.

The object of the present paper is to seek a similar relation from an equation of state of the type of van der Waals's equation.

Writing van der Waals's equation in the form

$$p+\frac{a}{v^2}=\frac{RT}{(v-b)}, \quad \ldots\ldots \quad (1)$$

we have by differentiation at constant pressure

$$\frac{1}{v}\left(\frac{dv}{dT}\right)_p\left[-\frac{2a}{v^2}+\frac{RT.v}{(v-b)^2}\right]=\frac{R}{(v-b)}. \quad \ldots \quad (2)$$

If this equation is applicable to the liquid state, the term $\frac{a}{v^2}$, which is the internal molecular pressure (intrinsic pressure of Laplace), is very large compared with the external pressure p, and hence

$$\frac{a}{v^2}\doteq\frac{RT}{v-b}. \quad \ldots\ldots \quad (3)$$

Making this substitution in (2), we readily find

$$\frac{1}{v}\left(\frac{dv}{dT}\right)_p=\frac{1}{\frac{a}{vR}-2T}. \quad \ldots\ldots \quad (4)$$

The quantity $\frac{1}{R}$ is proportional to T_c, the critical temperature of the liquid, and, assuming that the ratio of the

* Communicated by Prof. Alfred W. Porter, F.R.S.

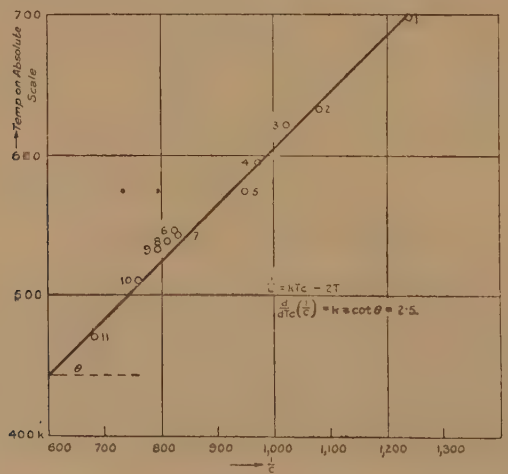
actual volume of the liquid occupied by the molecules to the total volume of the liquid is practically constant for liquids under ordinary conditions of temperature and pressure, equation (4) takes the form

$$\frac{1}{v}\left(\frac{dv}{dT}\right)_p = \frac{1}{kT_c - 2T}. \quad \ldots\ldots \quad (5)$$

If C denotes the coefficient of cubical expansion,

$$\frac{1}{C} = kT_c - 2T. \quad \ldots\ldots \quad (6)$$

To determine the numerical value of the constant k, a graph was drawn connecting $\frac{1}{C}$ with T_c for different liquids, as shown on the accompanying diagram; and the best straight line was drawn through the several points.



1. Aniline.
2. Xylol.
3. Amyl alcohol.
4. Toluol.
5. Bromine.
6. Carbon bisulphide.
7. Amyl alcohol.
8. Propyl alcohol.
9. Chloroform.
10. Acetone.
11. Pentane.

The graph shows that a linear relation of the type (6) represents with considerable accuracy the relation between the coefficients of expansion and critical temperature for liquids.

As indicated by the slope of the straight line, the numerical value of the constant k was taken to be 2·5; and equation (6), written in the following form, was used to

calculate the coefficient of expansion of liquids from known values of the critical temperature :

$$C=\frac{1}{kT_c-2T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The constants used in Table I. were taken from Landolt and Börnstein's tables and Kaye and Laby's tables.

In the case of substances which are solid at 0° C., C is calculated at the lowest temperature at which these substances are in the liquid state.

TABLE I.

Liquid.	Critical temp. in ° C.	$C=\frac{1}{2{\cdot}5T_c-2T}$	Experimental values of C.	Davies's formula, $C=\frac{1}{2T_c-T}$;
Pentane	197	·00155	{·001464 ·0016}	·001499
Ethyl alcohol ...	247	·00131	·00110	
Methyl alcohol ...	{232 240}	·00135	·00134	
Propyl alcohol ...	265	·00122	·00119	·00124
Alhyl alcohol ...	271·9	·00119	·00113	
CS_2	273	·00119	·00121	
Toluol	321	·00105	·001028	·001062
Chloroform	260	·00124	·00126	
Bromine.....	302	·00110	{·00104 ·001103}	·001167
Aniline	426	·000817	·00082	·000869
Xylol	358	·00099	·001016	·00101
Acetone	237	·00133	·001324	·001339
Amyl Alcohol ...	348	·00097	·00094	·00103

For purposes of comparison the values of C as given by Davies's formula are also shown in the table.

In calculating the value of C from equation (6), the integer nearest the known value of critical temperature has been used, and also where the tables gave values of critical temperature by different observers the mean value was used in the calculation.

From the agreement between the calculated values and observed values of coefficient of expansion, it would appear that the process of calculation could be reversed, and the equation (6) could be used for calculating the critical temperature if the coefficient of expansion is known. It is

assumed throughout that the coefficient is for a temperature remote from the critical value.

Relations similar to that expressed by equation (6) could be obtained by using Clausius's or Dieterici's equation of state.

It is also interesting to see how the equation (7) holds for liquefied gases, the pressure being sufficiently moderate, so that the assumption

$$\frac{a}{v^2} \doteq \frac{RT}{(v-b)}$$

in the derivation of equation (7) is valid.

TABLE II.

Coefficients of Expansion of Liquefied Gases.

Critical temp. in ° C.	Critical press. in atmospheres.	Liquefied gas in ° C.	C given by equation (7).	Experimental values of C.	Davies's formula, $C=\frac{1}{2T_c-T}$.
130	115	Ammonia −50 to 0	·00195	·00193 *	·00179
154·7	78·9	Sulphur dioxide − 50 to 0	·00174	·00170 *	·0015
31·1	73	Carbon dioxide −50 to 0	·00476	·00495 *	·00279
−118	50	Oxygen near −200	·00416	·00385 †	·00427
−146	33	Nitrogen near −200	·0058	·00558 †	·0052
−141	35·9	Carbon monoxide near −200	·0058	·00491 †	·0052
−117·4	52·9	Argon near −200	·0044	·00451 †	·0043
146	93·5	Chlorine −102 to −33	·00150	·001409 ‡	·00150
		− 30 to 0	·00178	·001793 ‡	·0016
		0 to 10	·00193	·001958 ‡	·0018

* Lange. † Baly and Donnan. ‡ Knietch.

The experimental data shown in Table II. are taken from Landolt and Börnstein's tables. In the case of chlorine (liquid state) the coefficient of expansion increases with temperature. This is also shown by the calculated values from equation (7) and those from Davies's formulæ.

Table III. shows the pressures of some of the liquefied gases at various low temperatures, showing how far the assumption

$$\frac{a}{v^2} \doteq \frac{RT}{(v-b)}$$

is valid in these cases.

TABLE III.

Liquefied gases.	Temperature ° C.	Pressure in atmospheres.	Observer.
Liquid CO_2 ...	−54	5·46	Cailletet.
	−54	4·6	
	−45	8·88	Faraday.
Liquid SO_2 ...	−10	1	Regnault.
	− 3·3	1·33	Faraday.
Liquid NH_3 ...	−30	1·14	Pictet.
	−15	2·28	

The external pressure p is only a few atmospheres as compared with the intrinsic pressure $\frac{a}{v^2}$, which in the case of liquids is of the order of thousands of atmospheres.

CIII. *The Refractivity of Gaseous Compounds.* *By* G. W. BRINDLEY, *M.Sc.*, *Demonstrator in Physics, University of Leeds* *.

1. *Introduction.*

IN a recent note to 'Nature' †, attention has been drawn to some simple relations which appear to exist between the refractivities of a number of gaseous compounds which, so far as the writer knows, have not been published elsewhere. The aim of the present paper is to discuss these relations and to consider how far similar arguments may be applied to other gaseous compounds.

2. *Survey of Previous Work.*

It has been generally observed ‡ that the refractivities of simple gaseous compounds do not follow an additive rule. Fajans and Joos §, using data obtained from the refractivities of solids, liquids, solutions, and gases, have shown that as

* Communicated by Prof. R. Whiddington, F.R.S.

† G. W. Brindley, 'Nature,' cxxiii. p. 165 (1929).

‡ In particular, Cuthbertson in a series of papers in the Proceedings and Transactions of the Royal Society, 1905–1914, in which accurate measurements of many gaseous refractivities are described, has considered the deviations from an additive law. Full references to Cuthbertson's work will be found in Proc. Roy. Soc. A, xcvii. p. 152 (1920).

Zeit. f. Physik, xxiii. p. 1 (1924).

the nuclear charge increases in a series such as O^{--}, F^{-}, Ne, Na^{+}, Mg^{++}, and Al^{+++}, where each member contains the same number of electrons, the refractivity decreases as the tightness of binding of the electrons increases. They consider that the refractivity of an atom or molecule depends mainly on the outer loosely-bound electrons, and that when combination occurs between atoms the conditoins governing the outer electrons are so much changed that an additive law does not hold. Born and Heisenberg* state that in hydrogen chloride the hydrogen nucleus penetrates into the electron shell surrounding the chlorine nucleus, thereby affecting the tightness of binding of the electrons in the chlorine ion, with the result that the refractivity of hydrogen chloride cannot easily be calculated.

Havelock† has treated the problem differently by using data derived from the intensity of light scattered transversely by a gas, and has calculated the refractivities of molecules containing two, three, four, and five atoms. In the case of hydrogen chloride, however, the calculated value of the molecular refractivity is 6·267 and the experimental value is 6·695; in the case of other gases the agreement is not any closer. For hydrogen chloride, Havelock concludes that "the difference . . . is a measure of the interaction of the two units," that is to say, of H^{+} and Cl^{-}.

So far, therefore, emphasis has been laid on the difference between calculated and observed values.

3. *Relations between Refractivities of some Gaseous Compounds.*

In Tables I., II., III., and IV., a number of simple relations are shown to hold fairly accurately between the refractivities of some simple gaseous compounds for a series of wave-lengths, λ. R(X) denotes values of $(\mu-1)$ for the substance X (corrected, as explained below), μ being the refractive index. It is usual to define the refractivity of a substance as $(\mu^2-1)/(\mu^2+2)$ for theoretical reasons, but for gases, where $(\mu-1)$ is small compared with unity,

$$\left(\frac{\mu^2-1}{\mu^2+2}\right) \doteqdot \tfrac{2}{3}(\mu-1).$$

Hence, in *comparing* refractivities it is justifiable to use $\mu-1)$ as a measure of the refractivity.

It is important to observe that for all the compounds

* *Zeit. f. Physik*, xxiii. p. 388 (1924).
† Phil. Mag. iii. pp. 158, 433 (1927).

considered the experimental values of the refractivities have been reduced to the values they would have had if the number of molecules per cubic centimetre of the gas or vapour had been equal to the number of molecules per cubic centimetre of hydrogen at 0° C. and 760 mm. pressure. Cuthbertson † has pointed out the convenience of expressing the experimental results in this way in preference to the older method in which they were reduced to 0° C. and 760 mm. pressure, because it enables the refractivities of different gases to be compared directly. The legitimacy of this method depends on the refractivity being proportional to the density and, for a given density, being independent of the temperature.

TABLE I.

$$R(HCl) = \tfrac{4}{7}R(Cl_2).$$

λ.	R . 10^6. (1) $R(Cl_2)$.	(2) $R(HCl)$.	(3) $\frac{4}{7}R(Cl_2)$.	Percentage difference between (2) and (3).
6707·8	77563	44375	44320	−0·1
6438·5	77703	44444	44400	
5790·5	78121	44656	44640	
5769·5	78135	44666	44648	
5460·7	78400	44800	44800	0
5209·1	78651	44930	44944	
5085·8	78791	45007	45024	
4799·9	79166	45187	45240	+0·1

Values of $R(Cl_2)$ and $R(HCl)$ obtained by C. and M. Cuthbertson, Phil. Trans. Roy. Soc. A, ccxiii. p. 1 (1914).

TABLE II.

$$R(CCl_4) = \tfrac{16}{7}R(Cl_2).$$

λ.	R . 10^6. (1) $R(Cl_2)$.	(2) $R(CCl_4)$.	(3) $\frac{16}{7}R(Cl_2)$.	Percentage difference between (2) and (3).
6708	775·63	1774	1772	−0·1
6438	777·03	1778	1776	
6104	779·02*	1782	1780	
5770	781·35	1791	1785	−0·3
5461	784·00	1799	1792	
5086	787·91	1810	1801	
4800	791·66	1819	1809	−0·5

Values of $R(CCl_4)$ obtained by H. Lowery, Proc. Lond. Phys. Soc. xxxix p. 421 (1927).

* Graphical interpolation.

† Proc. Roy. Soc. A, xcvii. p. 152 (1920); Phil. Trans. Roy. Soc. A, ccv. p. 323 (1905).

Table III.

$R(HBr)$ and $R(Br_2)$.

λ.	R . 10^6. (1) $R(Br_2)$.	(2) R(HBr).	(3) $\frac{1}{2}\frac{3}{5}R(Br_2)$.	(4) $\frac{4}{7}R(Br_2)$.	Percentage difference between (2) and (3)	(2) and (4).
6708	1152·5	607·5	599·2	658·3	−1·4	+ 7·7
6000	1166·2	611·1*	606·5	666·5	−0·8	+ 9·0
5800	1173·5	612·4*	609·5	670·0	−0·5	+ 9·4
5461	1184·9	614·9	616·0	677·0	+0·2	+10·1

Values of $R(Br_2)$ and R(HBr) obtained by C. and M. Cuthbertson, *loc. cit.*

* These values obtained by graphical interpolation.

Table IV.

$R(CS_2)=\frac{4}{3}R(S_2)$.

λ.	R . 10^6. (1) $R(S_2)$.	(2) $R(CS_2)$.	(3) $\frac{4}{3}R(S_2)$.	Percentage difference between (2) and (3).
6438	1099·3*	1443	1465	+1·54
5770	1113·2*	1464	1484	+1·36
5461	1120·5	1476	1494	+1·21
5086	1132·5	1495	1510	+1·00

Experimental values of $R(S_2)$ were obtained by C. and M. Cuthbertson, Proc. Roy. Soc. A, lxxxiii. pp. 167, 168 (1909), and lxxx. p. 411 (1908); and of $R(CS_2)$ by H. Lowery, Proc. Lond. Phys. Soc. xxxviii. p. 470 (1926).

* Graphical interpolations.

4. *Discussion of Relations between Refractivities.*

In Tables I. and II. the relations between $R(Cl_2)$, R(HCl), and $R(CCl_4)$ hold very closely indeed. In Table IV. the relation between $R(S_2)$ and $R(CS_2)$ does not hold so closely as the previous relations, but it is good compared with the kind of agreement previously obtained between calculated and observed values. The results given in Table III. are discussed in detail below.

The following relations form the basis of a tentative explanation of these results :—

$$(1)\quad \frac{R(HCl)}{R(Cl_2)} = \frac{4}{7} = \frac{\text{Number of M electrons in } Cl^- \text{ ion}}{\text{Number of M electrons in } Cl_2},$$

$$(2)\quad \frac{R(CCl_4)}{R(Cl_2)} = \frac{16}{7} = \frac{4 \times (\text{Number of M electrons in } Cl^- \text{ ion})}{\text{Number of M electrons in } Cl_2},$$

$$(2\,a)\quad \text{From (1) and (2)}\ \frac{R(CCl_4)}{R(HCl)} = 4,$$

$$(3)\quad \frac{R(CS_2)}{R(S_2)} = \frac{4}{3} = \frac{2 \times (\text{Number of M electrons in } S^{--} \text{ ion})}{\text{Number of M electrons in } S_2}.$$

In HCl the electron contributed to the molecule by the hydrogen atom completes an argon-like arrangement of electrons round the chlorine nucleus. Assuming that the hydrogen nucleus makes no contribution to the refractivity of HCl, that the K and L electrons are so tightly bound that their contributions to the refractivities of HCl and Cl_2 are small, and that the refractivities arise mainly from the loosely bound M electrons, then relation (1) follows, provided the binding of the M electrons is approximately the same in both molecules. Similarly, in the case of CCl_4 and also of CS_2, assuming the four outer electrons of the carbon atom, which are very loosely-bound, complete argon-like arrangements of electrons round the chlorine and sulphur nuclei, and that the binding of the M electrons in CCl_4 and CS_2 is approximately the same as in Cl_2 and S_2 *, then relations (2), (2 *a*), and (3) follow directly.

These results may be discussed on the basis of the quantum theory of dispersion developed by H. A. Kramers and W. Heisenberg †, according to which

$$\frac{\mu^2-1}{\mu^2+2} = \frac{4\pi}{3} \cdot \frac{Ne^2}{m} \left\{ \sum_{j>k} \frac{f_a}{\omega_{jk}^2 - \omega^2} - \sum_{j<k} \frac{f_e}{\omega_{jk}^2 - \omega^2} \right\}, \quad (1)$$

where the summations extend over possible transitions of electrons ; f_a is proportional to the probability of a transition due to absorption of energy, and f_e due to emission of energy. If the atom is in the ground state, f_e is zero. f_a is greatest for the outermost electrons which are most loosely bound. Hence, if in two different molecules the outer electrons are in similar energy and quantum states the value of f_a for such electrons will be proportional to their number, so that if these conditions are satisfied, simple relations of the kind observed would be expected.

* The sulphur molecule is assumed diatomic in the vapour state. *Cf.* C. Cuthbertson, Proc. Roy. Soc. A, lxxxiii. p. 151 (1909). B. Rosen, *Zeit. f. Physik*, xlviii. p. 545 (1928).

† Cf. *Zeit. f. Physik*, xxxi. p. 681 (1926).

These results may also be considered on the basis of the analogous expression given by the classical electron theory *, according to which

$$\frac{\mu^2-1}{\mu^2+2}=\frac{4\pi}{3}\cdot\frac{Ne^2}{m}\Sigma\frac{Z_p}{p^2-n^2}, \quad . \quad . \quad . \quad . \quad (2)$$

where Z_p is the number of quasi-elastically bound electrons of natural frequency p. If $p>>n$, the summation may be written $\Sigma\frac{Z_p}{p^2}$, and since p is smallest for the outer electrons, $(\mu^2-1)/(\mu^2+2)$ is proportional to Z_p.

In the case of HBr and Br_2 the same relation is not found between the refractivities which holds in the case of HCl and Cl_2, and a simple explanation is obtained from equations (1) and (2) above. In the case of bromine, there is absorption in the visible region of the spectrum, indicating that $p>>n$, so that a small change in p, which depends on the state of binding, may produce a large change in refractivity. Similarly for HI and I_2; iodine vapour has a large absorption in the visible region, and no simple relation is observed between the refractivities. In a note to 'Nature' † it was stated that the ratio of the refractivities of HBr and Br_2 is $(\frac{13}{25})$, which is equal to the ratio of the numbers of M and N electrons in the two molecules. Although the ratio $(\frac{13}{25})$ holds fairly accurately (see Table III.), since the M electrons in Br_2 and HBr are much more tightly bound ‡ than the N electrons, in view of the discussion above, it seems better to regard this agreement as a coincidence rather than as a statement of physical reality, and to consider that the "$(\frac{4}{7})$ relation" fails owing to absorption in the visible region.

In other molecules, where conditions are not so favourable as in HCl, Cl_2, and CCl_4, such simple relations are not found. In many cases, using arguments similar to those above, agreements can be obtained within 3 per cent. to 5 per cent., and in general the results are closer than those derived using an additive rule. It has not been thought worth

* *Cf.* O. W. Richardson, 'Modern Electron Theory,' 2nd ed. p. 148.

† *Loc. cit.*

‡ *Cf.* values obtained for a constant ϵ proportional to the total energy of an electron for the different electrons in Rb^+ ion. There are the same number of electrons in Rb^+ as in Br^- (*vide* D. R. Hartree, Proc. Camb. Phil. Soc. xxiv. p. 111 (1928)).

while to discuss these results, for it is clear that the method is only approximate. In molecules such as the oxides of nitrogen and of sulphur and in organic compounds, it is evident on general grounds that the distribution and binding of the electrons are characteristic of the molecule as a whole and not of particular atoms in the molecule. In the case of CH_4, for example, it is obvious that the same kind of argument cannot be applied which is used for CCl_4. It is of interest to note that results * obtained from the X-ray examination of the crystalline compound $C_6(CH_3)_6$, in which the (CH_3) group is of crystallographic importance, are in agreement with the view that this group cannot be regarded mainly as a distribution of charge about the carbon nucleus, in which the hydrogen nuclei have little influence, but that there is a certain distribution of charge determined more or less equally by all the nuclei.

5. *Summary.*

In previous papers attention has been directed to the discrepancies between calculated and observed values of gaseous refractivities. In the present paper four simple relations are given between the refractivities of gaseous compounds, these relations holding fairly accurately.

A tentative explanation is given based on the numbers of loosely bound electrons, and it is shown that, if certain conditions are approximately satisfied, such simple relations might be expected both from the quantum theory and also from the classical theory of dispersion. It is realized that a simple explanation of this kind cannot be final; a more detailed explanation is required which will be applicable in the general case.

In conclusion I wish to take this opportunity to thank Mr. Herbert Bell and Mr. R. G. Wood for assistance in reading previous work on this subject, and Prof. W. L. Bragg, F.R.S., and Dr. E. C. Stoner for valuable criticism and suggestions.

University of Leeds.
Feb 12, 1929.

* See a paper by Dr. Kathleen Lonsdale to be published soon by the Royal Society. I am indebted to Dr. Lonsdale for pointing out this interesting fact.

CIV. *Notices respecting New Books.*

Alternating Current Rectification. By L. B. W. Jolley. (Chapman and Hall, 11 Henrietta Street, Covent Garden, London, W.C. 2. Price 30*s.* net.)

THE revised edition of Mr. Jolley's work incorporates many of the important technical improvements in the design of rectifiers which have recently been made by British and foreign investigators. In addition to the types of rectifiers considered in the first edition, two or three supplementary chapters are devoted to wireless rectifiers and inverters. After consideration of valve and crystal rectification, it was natural that the question of high and low tension radio supplies should follow. The author deserves commendation rather than adverse criticism for the introduction of these important chapters. In the limited space at his disposal, the author has given the mathematical treatment required for the effective study of rectification. The bibliographies at the end of the chapters are of especial value for further study: references are given to original papers and to notices of these papers in Science Abstracts. Mr. Jolley's volume gives a comprehensive account of present-day practice and can be recommended as an up-to-date presentation of this branch of electrical engineering.

Statistical Mechanics with Applications to Physics and Chemistry. By R. C. Tolman. (The Chemical Catalog Company. New York, U.S.A. Price 5 $.)

This work, of special interest to students of chemistry, sets out the theory of statistical mechanics and discusses the many applications of this theory to both chemical and physical problems. The elements of the earlier quantum mechanics are introduced and applied to the particular cases of specific heats of gases and solids and the vapour pressure of crystals at very low temperatures. In addition to the chapters on molecular states and the absorption and emission of radiation, the author gives a very full treatment of the rates of physical and chemical processes, diffusion, evaporation, adsorption, solution, thermal and electrical conductivities. One chapter, based on the Arrhenius hypothesis of activation, is devoted to the temperature coefficients of reaction velocities. Attention is called to the inadequacy of the hypothesis, *e.g.*, in the classical experiment of Gerlach and Stern on the magnetic orientation of silver atoms.

The rate and change of rate with temperature of photochemical reaction are next considered and brief references made to the effect of external electric and magnetic fields on molecular systems. Prof. Tolman's volume gives an excellent survey of the latest investigations in this branch of science, will enable the reader to study with profit more advanced treatises, and in indicating

further directions of advance should promote research and assist in the development of this subject.

Materiewellen und Quantenmechanik, eine elementare Einführung. By Prof. Arthur Haas. (Leipzig: Akademische Verlagsgesellschaft, M.B.H. Price 8 marks.)

In 'Materiewellen und Quantenmechanik,' the author of the well-known 'Einführung in die theoretische Physik' has provided a concise and elementary introduction to the study of the theories associated with the names of de Broglie and Schrödinger. Eigen functions and Eigen values are illustrated by the simple cases of differential equations satisfied by Hermite's polynomials and Legendre's spherical harmonics, followed by application to the problems of Planck's oscillator and the hydrogen atom. The quantum mechanics of Heisenberg and the quantum statistics of Bose and Fermi are summarized, and brief references are given to the work of Dirac and others. The English translation of this excellent introduction to the modern theory of atomic dynamics will be appreciated by a wider circle of readers and deserves the favourable reception accorded to the authors' Introduction to Theoretical Physics.

The Chemical effects of Alpha Particles and Electrons. By S. C. Lind, Ph.D. [Second (revised and enlarged) edition.] (The Chemical Catalog Co. New York. Price 5 $.)

The new edition of Dr. Lind's work has soon followed the publication of the first: in its revised and enlarged form the author has surveyed the theoretical and experimental results which have been published during the last few years. Among the subjects included in this second edition are the researches of Mund on the action of radon on gases and the equation for calculating ionization in large spheres, a formula of great importance and practical application; the work of Erikson and Wahlin on ion clusters; the author's experiments on the acceleration of acetylene polymerization by nitrogen ions, and the discovery that even inert gases like helium, argon, etc., contribute to the reaction in exact proportion to their ionization. Experimental tests of photochemical equivalence are described with brief references to the work of Taylor, Dickinson, Bonhoeffer, and others. Two useful indexes of authors and subjects are appended.

Catalysis in Theory and Practice. By Eric K. Rideal and Hugh S. Taylor. (Macmillan & Co. Ltd., St. Martin's Street, London. Price 20*s.* net.)

The first edition of this book appeared some nine years ago and received an appreciative notice in the pages of this Magazine. The volume of research in the theory and application of catalysis has expanded considerably since the publication of the first edition: the second edition, revised and enlarged, incorporates

recent contributions to the study of catalysis, including the numerous researches of the two authors. This has necessitated the addition of new sections: as far as it is possible in this rapidly growing branch of chemical science, other chapters have been brought up to date. It is not without interest to note the association of the Philosophical Magazine with the progress made in the study of catalysis during the last hundred years. Nearly a century ago, papers were published by Faraday on his theory of passivity, by Henry on the combustion of carbonic oxide, and by Draper on photochemical reactions. Recently, contributions have been made by several research workers, including R. W. Wood, Rideal, Hinshelwood, and others.

Sound, a Physical Text-book. By E. G. Richardson, B.A., M.Sc., Ph.D. (Edward Arnold and Co., 41 & 43 Maddox Street, London, W. 1. Price 15*s.* net.)

Dr. Richardson's text-book is a welcome addition to the literature dealing with the subject of experimental acoustics. The results of recent experimental researches are reviewed and include the extensive work of Raman on the bowed string and of W. H. George on the struck string to discriminate between the Helmholtz and Kaufmann theories: some sections on various types of musical instruments are also included.

An elementary introduction to the theory of Prandtl on the motion of viscous fluids is followed by the discussion of eddies and vortices and Kármán's experimental verification for maximum stability. Under the heading of technology, the investigations of Sabine, Jäger, and others on the acoustics of buildings are noted, as well as the problems of sound ranging, direction finding, and other technical applications. Numerous references are given to original papers, especially those which have appeared during the last few years. A great amount of information is brought together in this book which will be of service both to degree students and research workers in this subject.

Alkaline Accumulators. By J. T. Crennell, B.A., and F. M. Lea, M.Sc., A.I.C. [Pp. x + 132, with 24 figures.] (London: Longmans, Green and Co. 1928. Price 10*s.* 6*d.* net.)

On account of their mechanical robustness, suitability for varied and intermittent use, and freedom from injury by overcharging, alkaline accumulators possess distinct advantages over acid accumulators for such purposes as train lighting, electric traction, wireless batteries, or for any other purpose in which the regular charging and discharging which is necessary to maintain acid batteries in good condition is not possible. They are a comparatively recent development, and their advantages have not been as generally appreciated as they should be.

The volume under review should do much to counteract this state of affairs. The methods of construction of cells of the

Edison and Jungner types are explained, together with their advantages and disadvantages, and methods of operation and maintenance. The theory of the action which takes place on charge and discharge is carefully explained and attention is drawn to gaps in the theory. A fair balance between theory and practice has been preserved, and the volume is one which all who use alkaline accumulators should possess. It is to be hoped, moreover, that its publication will stimulate research in those directions in which the theory is still obscure.

Symbols and Formulæ in Chemistry. By R. M. Caven, D.Sc., F.I.C., and J. A. Cranston, D.Sc., A.I.C. [Pp. ix+220.] (London: Blackie and Son. 1928. Price 15*s.* net.)

In this volume is given an account of the use of symbols in chemistry from the beginnings of the science down to the present day. Many of the early symbols are of no scientific value but are quaint or amusing and of antiquarian interest. The historical account of the beginnings of symbolism embodies the results of extensive research. The gradual development of modern symbols is traced and the application of theories of structure to structural formulæ is considered. Other subjects treated include an account of the development of stereochemistry, theories of valency, and the electron in chemistry. There is no reference to the important application of X-ray methods of analysis to the elucidation of the structure of crystals and of organic substances. The volume provides a general survey of great interest to the student of chemistry and of considerable value for purposes of reference.

The Theory of Determinants, Matrices, and Invariants. By H. W. Turnbull, M.A. [Pp. xvi+838.] (London: Blackie and Son. 1928. Price 25*s.* net.)

The first seven chapters of this book deal with the theory of determinants and of matrices, written mainly with a view to their applications in the remainder of the book. The theory of binary forms is then considered briefly, serving as an introduction to general and multilinear forms and the general properties of invariants. The applications of the theory to algebraic and differential geometry have been omitted, as well as the algebra of alternate numbers. An account is given of the more important recent work on the subject, including Weitzenböck's account of the basis of analytical projective geometry in relation to the usual metrical forms.

Both the direct and the symbolic methods are explained and used. The volume provides an excellent introduction to the subject, is well printed, and contains a number of illustrative examples. Recent developments in physics have attracted increased attention to the theory, and the publication of the volume comes at an opportune time.

1. *Untersuchungen zur Quantentheorie* von Louis de Broglie. *Übersetzt* von Dr. W. Becker. [Pp. iii+88, with 6 figures.] (Leipzig: Akademische Verlagsgesellschaft M.B.H. 1927. Preis M.5.80.)

2. *Four Lectures on Wave Mechanics.* By Dr. Erwin Schrödinger. [Pp. viii+53.] (London; Blackie and Son, Ltd. 1928. Price 5*s.* net.)

3. *Collected Papers on Wave Mechanics.* By E. Schrödinger. Translated by J. F. Shearer, M.A., B.Sc., and W. M. Deans, B.A., B.Sc. [Pp. xiii+146.] (London: Blackie and Son, Ltd. 1928. Price 25*s.* net.)

4. *Selected Papers on Wave Mechanics.* By Louis de Broglie and Léon Brillouin. Translated by W. M. Deans, B.A., B.Sc. [Pp. viii+151.] (London: Blackie and Son, Ltd. 1928. Price 15*s.* net.)

Wave Mechanics as developed by Schrödinger, starting from ideas put forward by de Broglie, has attracted much attention in view of the success which it has achieved in explaining many quantum phenomena without introducing the idea of discontinuity. The theory is based on the analogy between the path of a ray of light and the path of a material particle: for dimensions comparable to the wave-length of light, the laws of geometrical optics no longer hold and undulatory optics must be used. Similarly, for dimensions comparable to the size of an atom, Newtonian dynamics no longer holds. Wave mechanics analogous to undulatory optics must be used.

(1) is a German translation of the original memoir of de Broglie, which appeared in *Annales de Physique*, 10, iii. This important paper is not included in (4), and those who read German with facility will welcome its republication in self-contained form.

(2) contains the substance of four lectures delivered at the Royal Institution in March, 1928. No better introduction to the theory can be recommended. This small volume is a masterly example of clear exposition, and in a few pages many of the successful applications of the theory are sketched.

(3) contains the translation of nine original papers by Schrödinger, which appeared during 1926 and 1927, arranged in chronological order. The study of this volume should follow the reading of (2). The papers have been reprinted without alteration, and it is of interest to follow the gradual development of the author's ideas. A somewhat detailed abstract of the contents, with references to the subsequent pages, enables the general line of thought to be clearly followed. The four principal papers on "Quantisation as a Problem of Proper Values" contain the main formulation of the theory. Another paper, entitled "On the Relation between the Quantum Mechanics of Heisenberg, Born, and Jordan, and that of Schrödinger" illustrates the close

relationship between wave mechanics and matrix mechanics, in spite of the widely differing initial assumptions.

(4) contains the translation of five original papers by de Broglie and of four by Brillouin which appeared, with one exception, during 1926 and 1927. Some of these papers summarize the investigations of de Broglie and Schrödinger and elaborate the connexion between wave and matrix mechanics. Of particular interest are the last two papers :—In "The Wave Mechanics and the Atomic Structure of Matter and of Radiation," de Broglie deals with the difficulty of reconciling the propagation of the waves of continuous amplitude of Schrödinger's wave mechanics with the atomic structure of matter and of radiation. He shows that continuous solutions provide only a certain statistical view of dynamical phenomena, the exact description of which probably requires the consideration of waves which admit of singularities. In "A Comparison of the Different Statistical Methods applied to Quantum Problems," Brillouin considers the differences between classical statistics and the methods of Bose and Einstein and of Fermi and Dirac; on certain assumptions the laws of emission and absorption of light stated by Einstein and their various generalizations are obtained.

CV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 760.]

February 20th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

THE following communication was read:—

'The Basal Complex of Jamaica, with special reference to the Kingston District.' By Charles Alfred Matley, D.Sc., F.G.S. With Petrological Notes by Frank Higham, B.Sc., A.R.S.M., F.G.S.

The author deals with the problem of the age of the old rocks of Jamaica, in the light of the results of detailed stratigraphical work in the Kingston district. The geological surveyors in 1859–66 recognized no rocks older than Cretaceous, and regarded the Jamaica 'granite' as Tertiary; and the same views were strongly expressed by R. T. Hill in 1899.

In the Kingston district and the country east of it the author finds a Basal Complex of great thickness, unconformably underlying Upper Cretaceous and Eocene rocks. The 'granite and syenite' of the Survey—chiefly a granodiorite—does not penetrate

the Tertiary 'White Limestone', as has been asserted, but is an important plutonic member of the Basal Complex, and contributes abundant pebbles to overlying Upper Cretaceous and Eocene conglomerates. Another plutonic member of the Complex is a peridotite of Harzburg type, now converted to serpentine.

The other members of the Complex, many of which are found in a metamorphic condition, were originally sediments and volcanic lavas and tuffs. They include marbles, schists of varied composition, amphibolites, granulites, and hornfelses. The schistose structure is chiefly the result of dynamic metamorphism acting on a series of limestones, calcareous mudstones, shales, sandstones, basic lavas, and tuffs. The less altered lavas and intrusives range from acid to basic. There is evidence that the contact-altered granulites and hornfelses had suffered from earth-movement before the granodiorite invaded them. As the metamorphism antedates Upper Cretaceous time, it is suggested that it is late-Palæozoic (Hercynian) or even older. No trace of fossils has been found in the Complex.

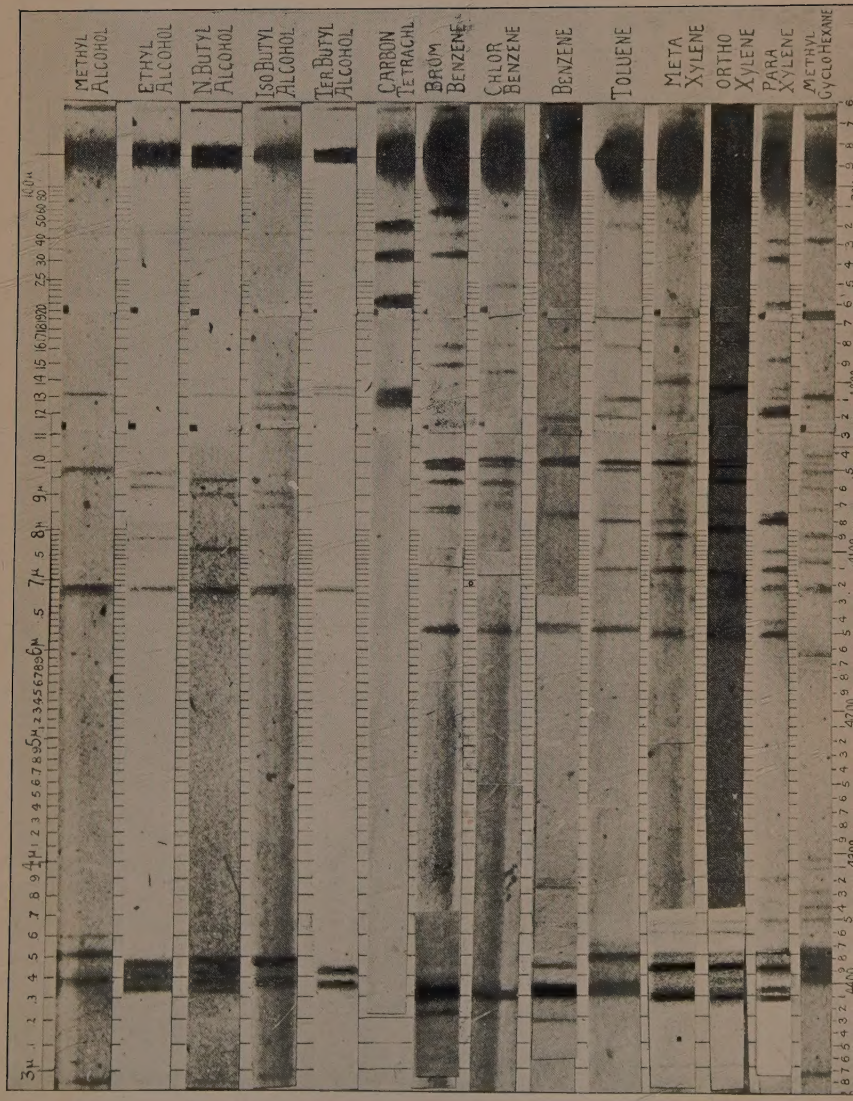
The rocks of the Complex have been involved with Upper Cretaceous and Eocene strata in the later (Tertiary) movements that formed the Blue Mountains, and their separation from the latter needs detailed field examination, owing to the complicated stratigraphy. For example, a lenticular strip, $3\frac{1}{2}$ miles long, in the Upper Yallahs valley, has been brought up on a thrust-plane and driven east-north-eastwards over a sigmoidal fold of Eocene rocks. Mylonization is traced along this thrust and elsewhere.

A group of red-weathering andesitic lavas and tuffs, with associated intrusives, are described. They underlie the Upper Cretaceous conglomerates, but it is not yet known whether they are of Cretaceous age or belong to the Complex.

Comparison is made with similar rocks in Cuba, Hispaniola (Haiti and Santo Domingo), Porto Rico, and the Virgin Islands. The asserted absence of pre-Cretaceous rocks in Porto Rico is discussed. With the exception of Porto Rico, Jamaica now falls into line, as regards the presence of a pre-Cretaceous basement, with the other islands of the Greater Antilles, although there is still want of agreement as to the ages of the rocks of that basement.

In the Appendix Mr. Higham deals with the petrology of the Complex, and compares the major intrusives with those in the other islands of the Greater Antillean group, in which the igneous history is very similar. The serpentines are regarded as earlier intrusions, the later activity being accompanied by intrusions of the calc-alkaline suite characteristic of the Andes. Evidence of consanguinity is also afforded by the constancy of titanium-minerals and the presence of clear colourless augite, which is often the primary mineral in the granodiorites.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]


Methyl Alcohol
Ethyl Alcohol
N.Butyl Alcohol
Iso Butyl Alcohol
Ter Butyl Alcohol
Carbon Tetrachl
Brom Benzene
Chlor Benzene
Benzene
Toluene
Meta Xylene
Ortho Xylene
Para Xylene
Methyl Cyclohexane